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TRIMETHYLENE INTERMEDIATES AND THE ADDITION OF SINGLET METHYLENES TO OLEFINS

BY

© LATIF H. ALI

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE

DEGREE OF MASTER OF SCIENCE

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled TRIMETHYLENE INTERMEDIATES AND THE ADDITION OF SINGLET METHYLENES TO OLEFINS submitted by Latif H. Ali, in partial fulfilment of the requirements for the degree of Master of Science.

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All financial assistance received from the University of Alberta is gratefully acknowledged.

Finally, the author deeply appreciates the friendship of all his fellows in the Chemistry Department, especially those in his research group.

ABSTRACT

Four 1-pyrazolines have been synthesized by the stereospecific cycloaddition of diazomethane to an olefin. They are cis and trans-3,4-dimethyl-1-pyrazoline and their -5,5-dideuterio analogues.

The kinetic behaviour and the distribution of the products in the thermal decomposition of the pyrazolines have been examined. It is concluded that the substituted trimethylene intermediate, which is a singlet, exists as an entity in the thermal decomposition of the 1-pyrazolines.

On the basis of the calculations, from the nmr integrations of the component 2-methyl-2-butene obtained from the thermolysis of the pyrazolines, it was concluded that ring closure was not stereospecific.

The conclusions drawn from previous work has been supplemented by the stereospecific synthesis of 2-methyl-2-butene-1,1,1,3-d_4 for the purpose of exact nmr assignment of the various methyl groups.

It is concluded that the singlet trimethylene species produced from pyrazoline thermolysis is not an intermediate in the addition of singlet methylene to olefins.

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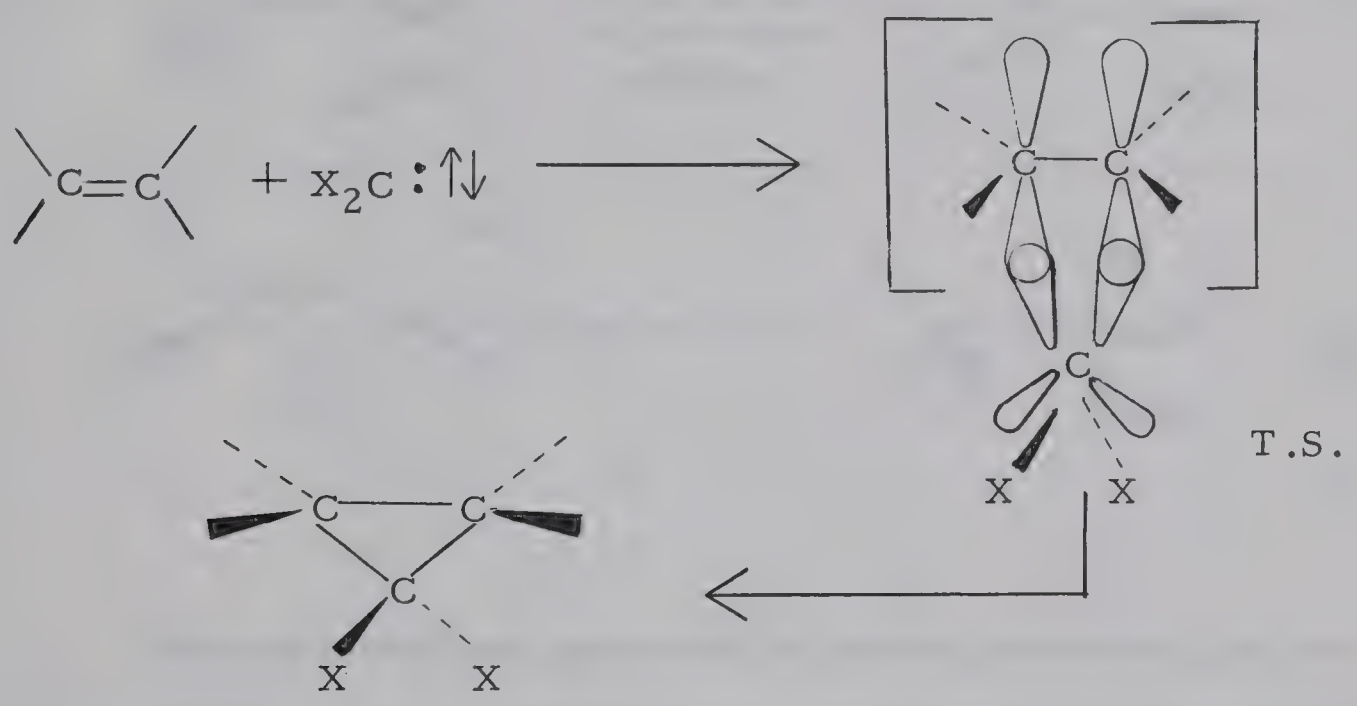
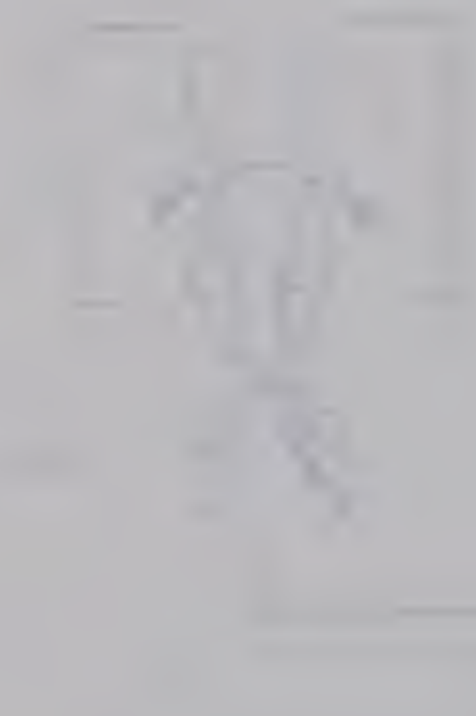
INTRODUCTION

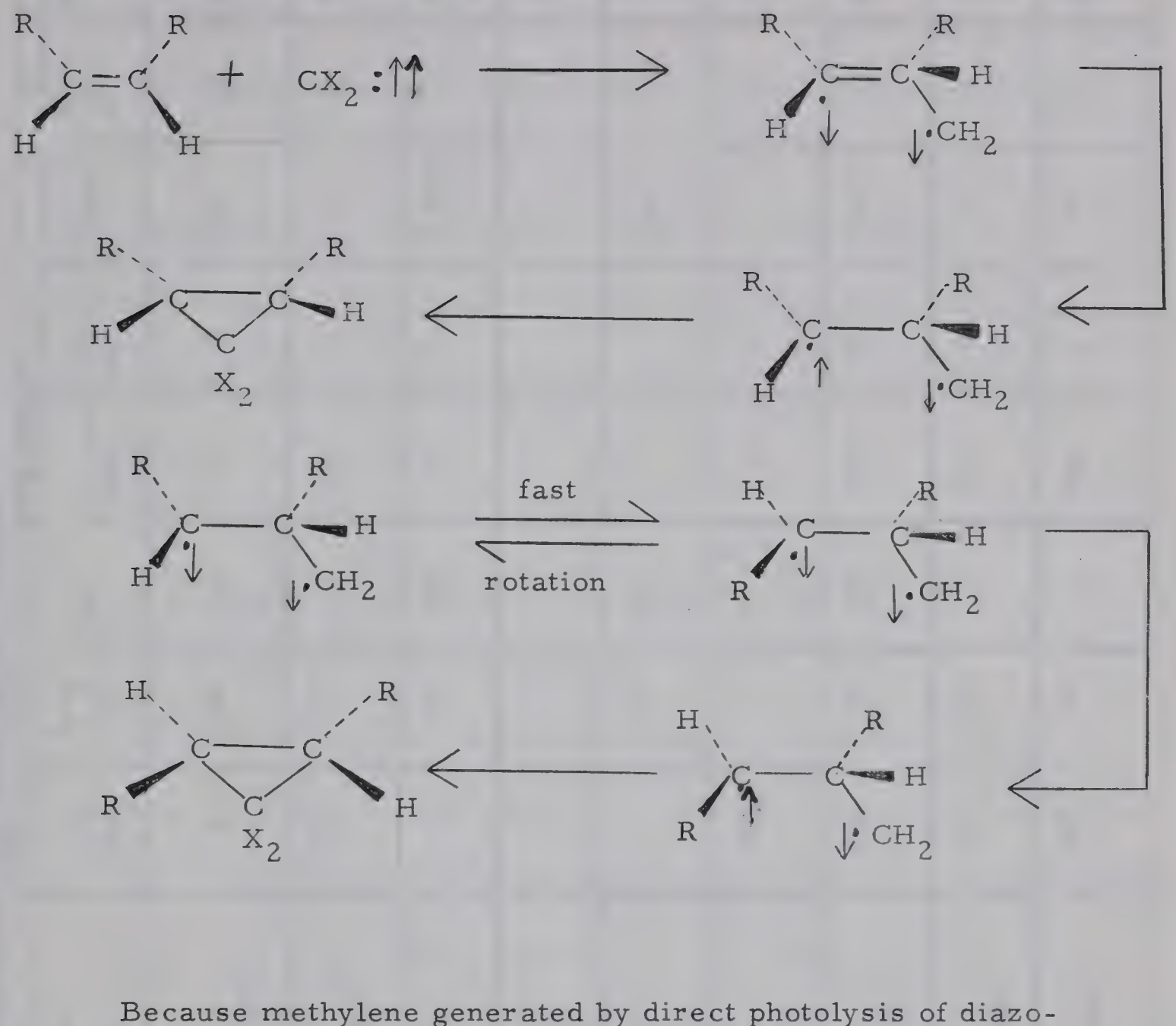
Skell[1] was the first to suggest a mechanism for the addition of methylene to double bonds. Singlet methylene might add to a double bond in a single three-centered concerted step since such a step could occur with spin conservation:



Conversely, it was reasoned that addition of a triplet might be expected to involve the separate bond-making processes, with spin inversion being a discrete intermediate step.

Since spin inversion is expected to be slow, it was presumed that single bond rotation in the intermediate would destroy the steric relationships originally present in the olefin:



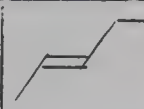
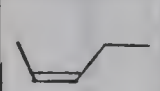
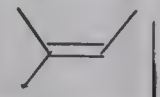
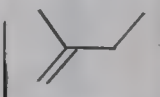
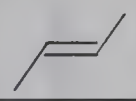
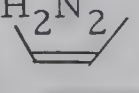
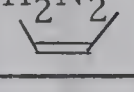
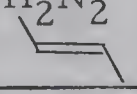
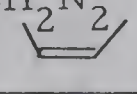


Because methylene generated by direct photolysis of diazomethane adds stereospecifically to alkenes, as shown by Skell and Woodworth[1], and Doering and La Flamme[2], it has been inferred that a singlet species is involved. Some of the data leading to this conclusion are to be found in Table I.

Methylenes produced by irradiation of diazomethane in the vapor phase in the presence of a high pressure of inert gas gives non-stereospecific addition to the 2-butenes as shown by Anet, Bader and Van derAuwere[3], and also by Frey[4]. Similar results were

TABLE I

Singlet Methylene Addition to cis- and trans-2-butene.

Source :CH	Press. (Torr)	Temp. °C	Mixture	PERCENT							Ref.
											
CH_2N_2 $h\nu$	10	25	1:12 CH_2N_2 : 	5	<20	40	7	-	20	15	6b
CH_2N_2 $h\nu$	10	25	1:12 CH_2N_2 : 	10	12	-	32	-	-	-	6b
CH_2N_2 $h\nu$	liq.	-70	dil. CH_2N_2 	-	51	40	-	-	9.2	-	15
CH_2N_2 $h\nu$	liq.	-70	dil. CH_2N_2 	-	-						15
CH_2N_2 $h\nu$	liq.	-75	dil. CH_2N_2 	-	27	59	-	-	14	-	2
CH_2N_2 $h\nu$	liq.	-75	dil. CH_2N_2 	99	-	-	-	-	-	-	2
CH_2N_2 $\triangle$	5	400	1:10 CH_2N_2 : 	20	15	10	35	3	20	3	16
CH_2N_2 $\triangle$	5	300	1:10 CH_2N_2 : 	20	15	5	40	1	15	1	16
CH_2N_2 $\triangle$	5	250	1:10 CH_2N_2 : 	30	15	3	40	1	15	1	16

obtained by Kopecky, Hammond and Leermakers[5] when methylene was produced by triplet sensitized photolysis in solution by using benzophenone.

Interpretation of all the above results have been based on Skell's hypothesis. Sensitized reactions should produce the triplet species. Skell's hypothesis has been questioned for the following reasons:

(a) Lack of a firm basis for the presumption that rotation about single bonds will necessarily be much more rapid than spin inversion.

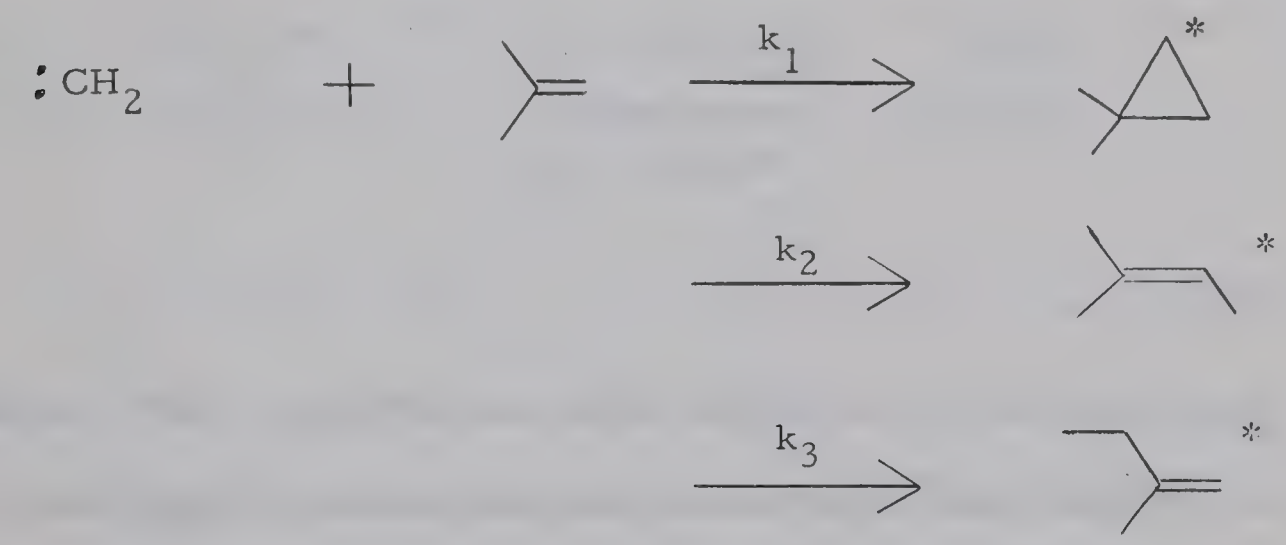
(b) It is not at all certain that addition of singlet methylene to a double bond must be a one step process just because it might be without violating spin conservation (consequently one could readily conceive of both stereospecific triplet addition and non-stereospecific singlet addition).

(c) Finally as was clearly pointed out by Frey[6], the cyclopropane formed by addition of singlet methylene to an alkene with conservation of energy would be "hot" enough to undergo a variety of isomerization reactions if it were not deactivated rapidly and efficiently.

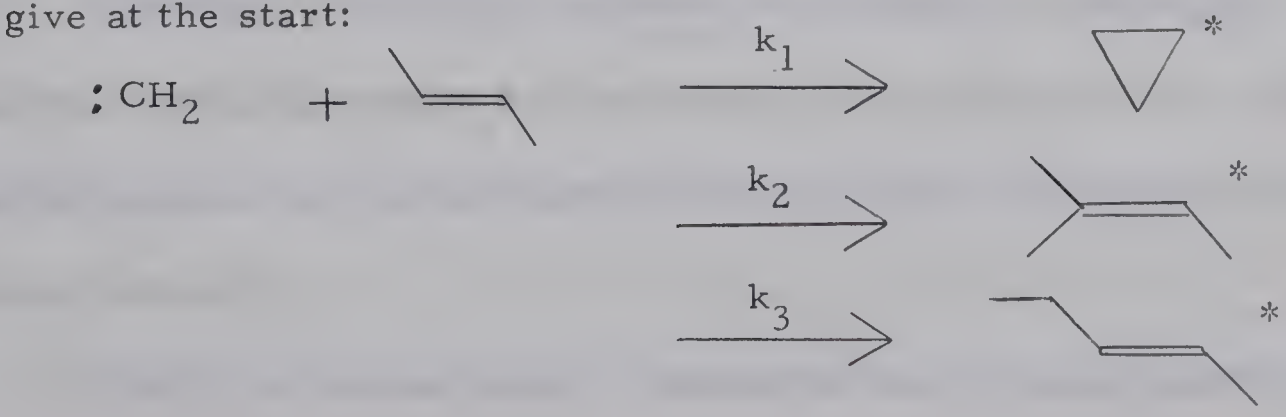
Butler and Kistiakowsky[7] have studied the addition of methylene to cyclopropane. Methylene was generated from diazomethane and from ketene at various pressures with and without added inert gases.

They obtained all the isomerization products and not just methylcyclopropane. When the system was cooled to the equilibrium state they found that the ratio of butenes to methylcyclopropane decreased as the pressure was increased (more deactivation by collisions). They also obtained more butenes when methylene was generated from diazomethane, thus it is expected to be in a higher state of excitation than that produced from ketene photolysis.

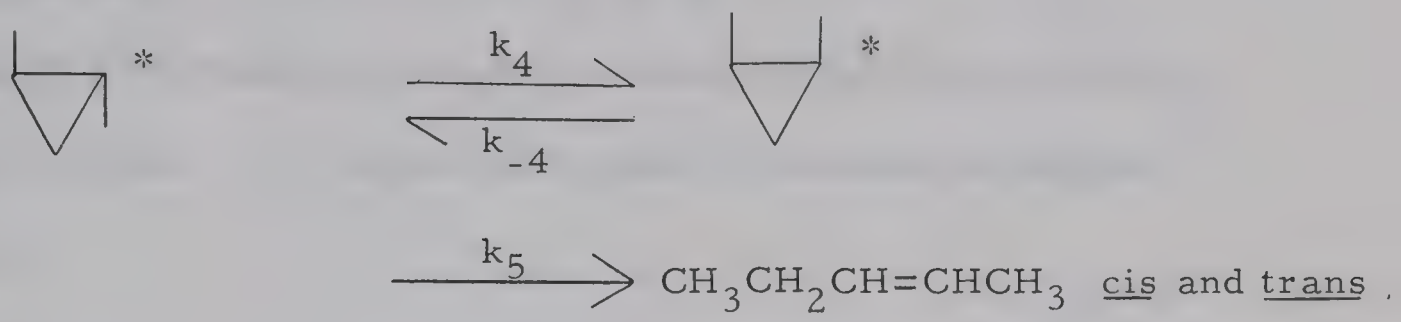
Frey[6] studied the effect of inert gas on the reaction of methylene with isobutylene. He came to the conclusion that the attack of methylene on the isobutylene initially forms three products:



In the same way, he considers the attack of methylene on trans-2-butene to give at the start:



and in the gas phase the hot trans-1,2-dimethylcyclopropane (DMC) can isomerize to:



Similarly "hot" cis-DMC can either isomerize or be deactivated. Hot cis- and trans-2-pentene can also isomerize to each other or be collisionally deactivated. Hot 2-methyl-2-butene will not give isomerization under these conditions.

That the yield of cis- and trans-1,2-DMC goes through a maximum as the pressure decreased was accounted for by the assumption that the geometrical isomerization is much faster than structural isomerization[6].

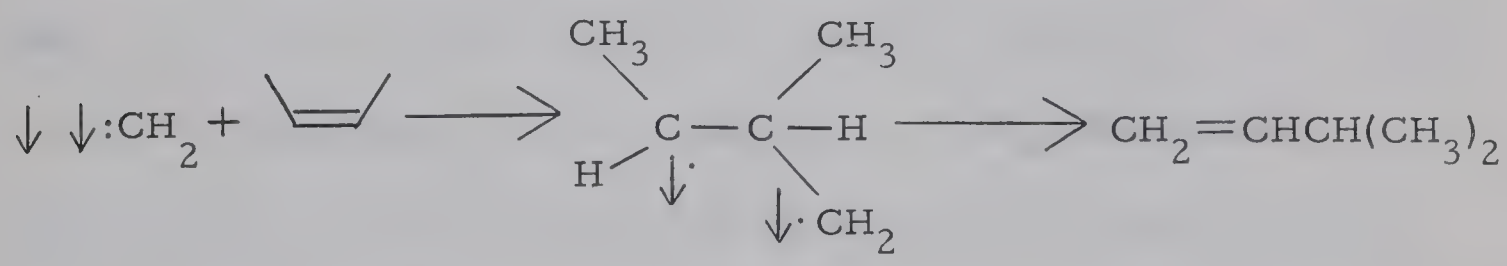
Frey[4], in another paper, claimed to have obtained another effect

of inert gas on the reaction, and that is:

i.e. change of spin state prior to the reaction of methylene with the olefin, cis-2-butene. At low pressure and in presence of oxygen, he obtained:

3.6% 50.9 0.9 27.7 1.8 15.0

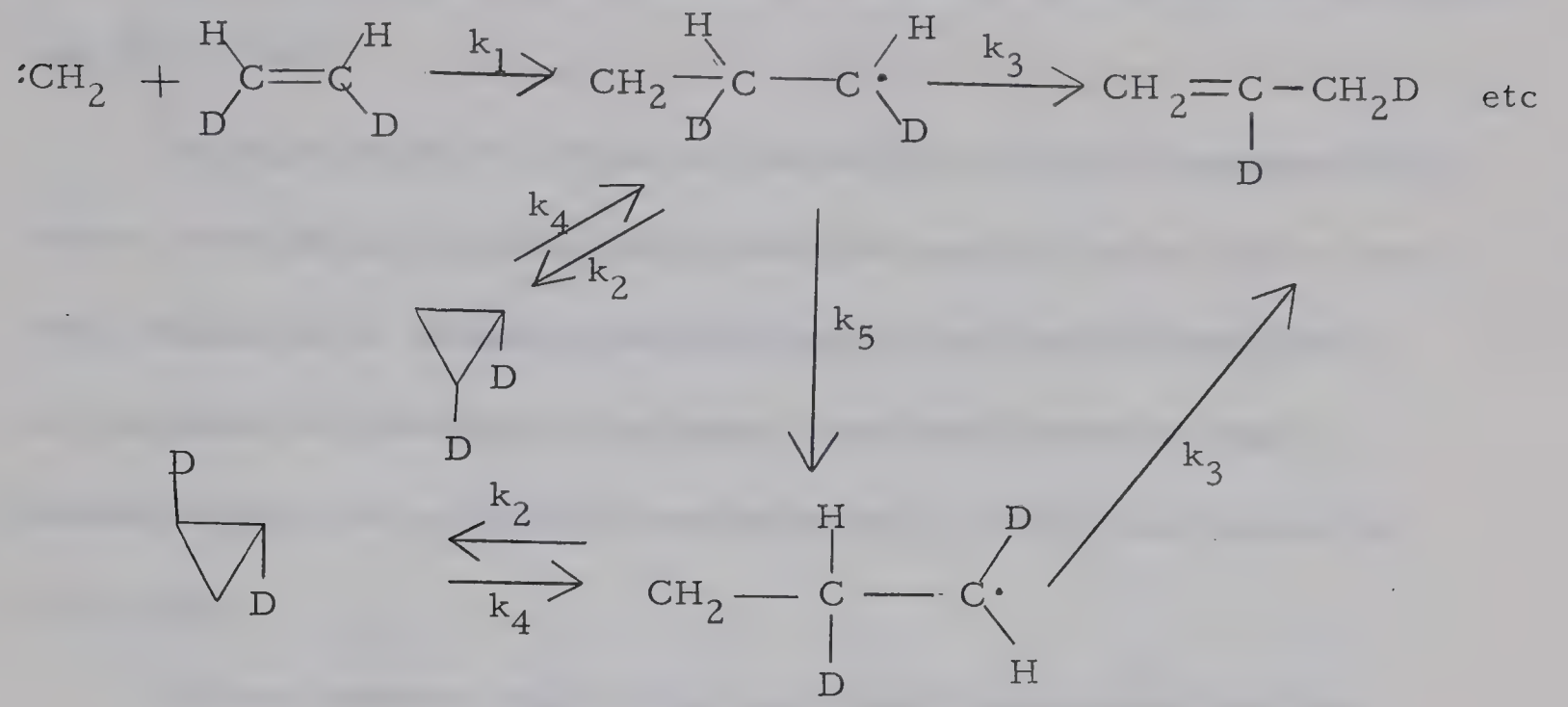
The most important product was 3-methyl-1-butene. This species cannot be formed by direct insertion, but must arise from rearrangement of some primary product, for example:



Rabinovitch[8] measured the relative amounts of cyclopropane-cis-d_2 and cyclopropane-trans-d_2 and propylene formed at various total pressures. The ratio of ketene/ethylene in this experiment was kept constant, so that the average degree of thermalization of methylene before reaction with ethylene should be constant. At high total pressure, the amount of propylene produced was constant and about fifteen percent. The yield of trans-cyclopropane-d_2 approaches zero at high pressure, but still changes significantly at 2000 mm, where

the propylene yield was reduced to its limit value.

Benson [9] has attempted to fit the data to the mechanisms:



The kinetic parameters from thermal isomerization of cyclopropane are:

Reaction	log A	E_a (kcal/mole)
2	13.0	8.2
3	12.2	9.5
4	16.0	64.5

Benson demonstrated that the relative rates of ring closure, rotation, and rearrangement to propylene can be estimated for any presumed energy content of the trimethylene diradical using the Rice-Ramsberger-Kassel[10,11] Theory:

$$k = A\left(\frac{E - E_a}{E}\right)^{n-1}$$

n = number of internal degrees of freedom = 12

E = exothermicity of addition + nRT

He found $E \simeq 25.5 + 7.2 \simeq 32.7$ at 300°, and thus at $300^{\circ}K$ he demonstrated that $\frac{k_2}{k_3} = 10^2$.

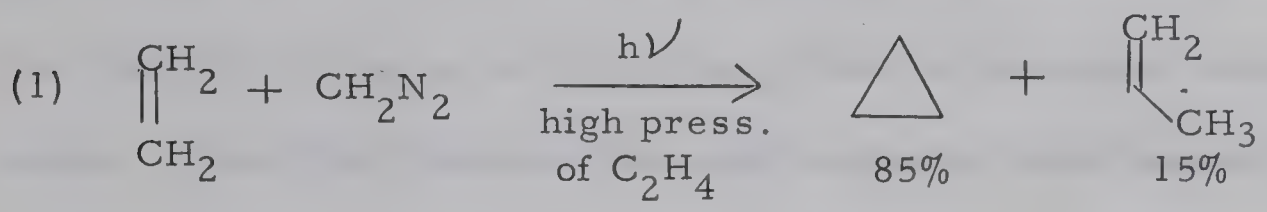
At high pressure, where no reopening of the cyclopropane will occur, the yield of propylene might well be expected to be 10% or less. This conclusion is certainly compatible with the data of Rabinovitch, and suggests the possibility that some propylene formed at high pressure might come from a diradical as well as by direct attack on C-H bonds.

At low pressure much propylene would be produced both by rearrangement of the initially formed diradical, and by reentry of the cyclopropane into the reaction scheme via reaction 4.

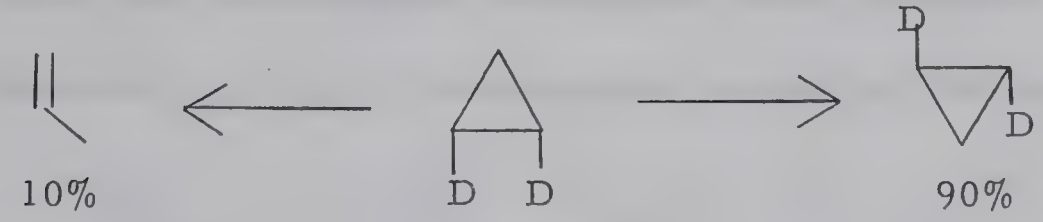
However, it was argued that this was no solution to the problem, since about 50% of the propylene must come from cyclopropane at the low pressure limit, one thus is left to decide whether cyclopropane preceeded the diradical or vice versa. Benson and De More[9] maintain that if the rate of rotation of the diradical is low enough, stereospecific ring closure would occur. Hammond and Gaspar[12] argued this point and stated that they cannot see how kinetic parameters for the rotation process can be chosen so as to make this a real possibility. They believe that stereospecific addition in the vapor phase demands that addition involves simultaneous formation of two bonds. Such a reaction could only be an adiabatic process if the attacking species is

a singlet.

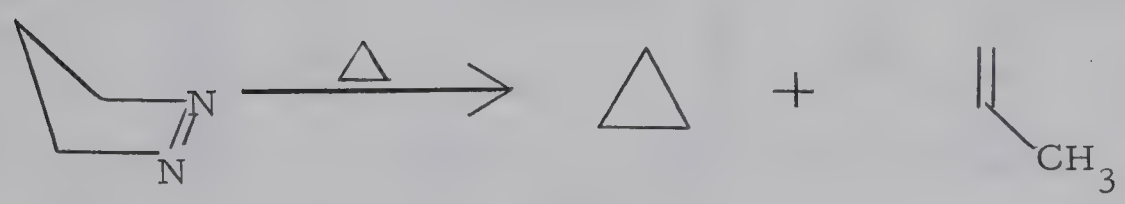
The purpose of our work is to correlate the mechanisms involving thermolysis of 1-pyrazolines, isomerization of cyclopropanes and singlet methylene addition to double bonds. The factors controlling the stereospecificity of the pyrazoline thermolysis products are established. The same factors are suggested to control those of cyclopropane isomerization and singlet methylene addition to double bonds may also be in this category since:

(1) 

Ref. 8

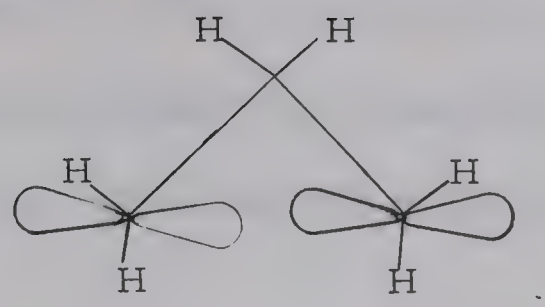
(2) 

Ref. 8

(3) 

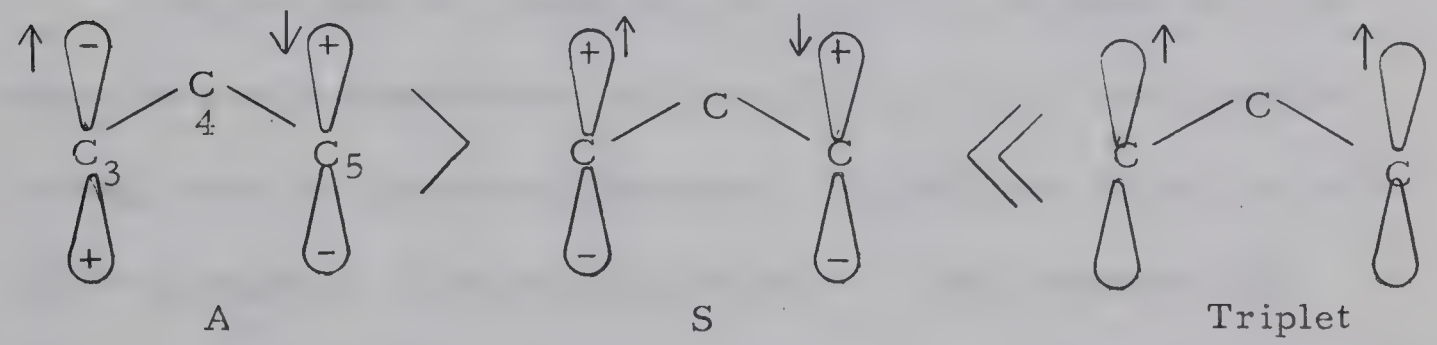
Ref. 13

A singlet methylene is expected in reaction (1), an isomerization in reaction (2), and (3) is a thermolysis reaction where a singlet trimethylene is expected as an intermediate. The similarity of the yields of the three processes suggests that all three may proceed through a common intermediate. Crawford and Mishra [13] have suggested that reaction (3) goes to the products through the species:



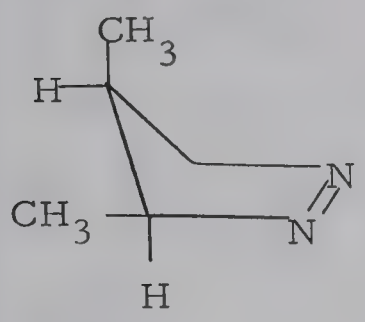
They demonstrated feasibility of that intermediate on the basis of the isotope effect when they put deuterium on the C_4 position of the 1-pyrazoline molecule. The isotope effect was a secondary one on the rate-determining step, and a primary one on the product-determining steps. They also observed that conrotation is more favored than disrotation when the intermediate rearranges to the products.

However, there are three possible states for the intermediate:

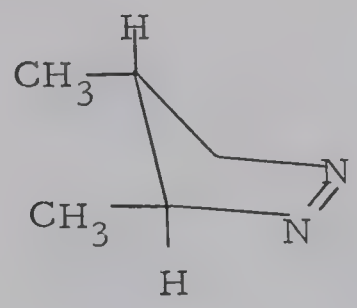


Hoffmann[14] has concluded from extended Hückel molecular orbital calculations that the antisymmetric species (A) is more stable than the symmetric one (S), and exists with a $C_3C_4C_5$ bond angle of approximately 120-125°. This is advantageous in that it is the predicted species from orbital symmetry considerations of the pyrazoline thermolysis process and is capable of explaining the prevailing conrotation for the cyclopropane-forming reaction, as observed by

Crawford and Mishra[13]. The nature of the intermediate of the thermolysis of cis-3,4-dimethyl-1-pyrazoline (I), and trans-3,4-dimethyl-1-pyrazoline (II) is thus suggested to be a singlet species, and antisymmetric.



(I)



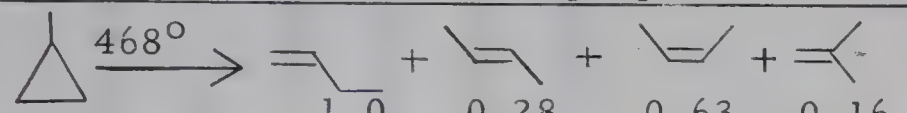
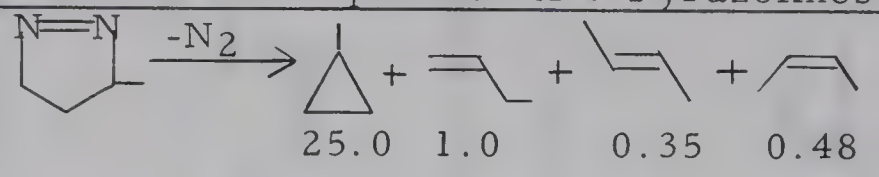
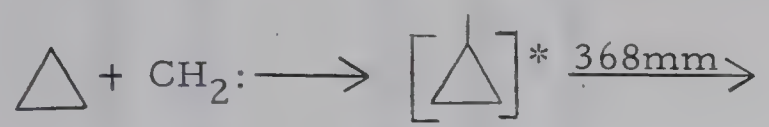
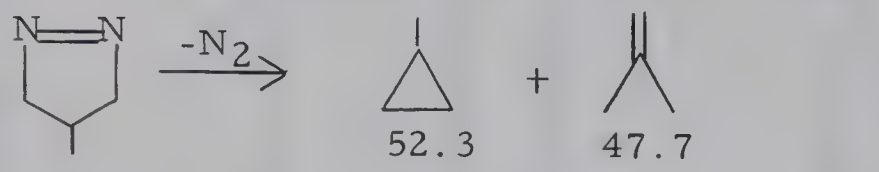
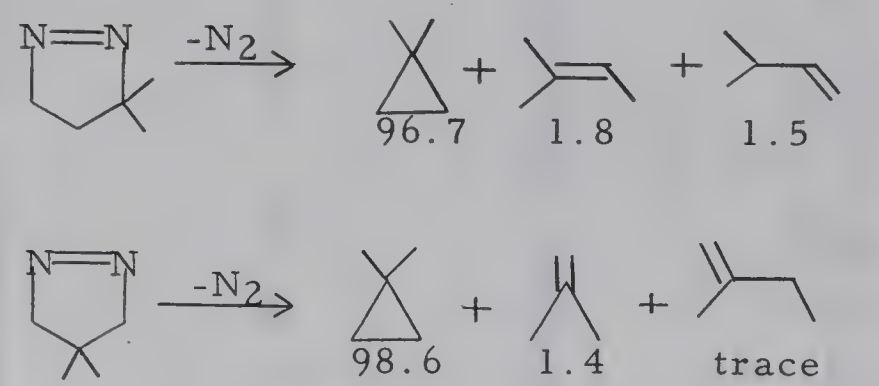
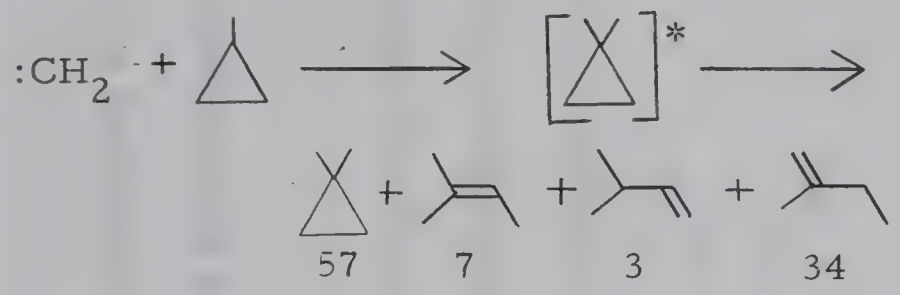
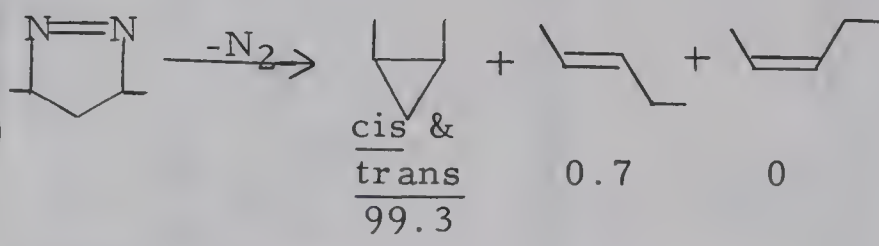
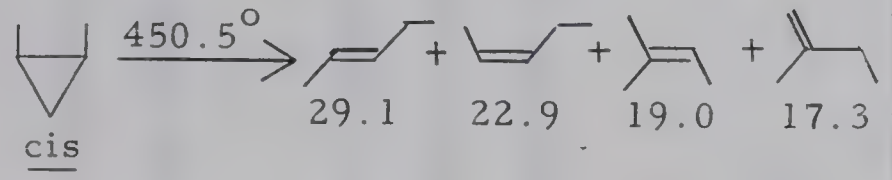
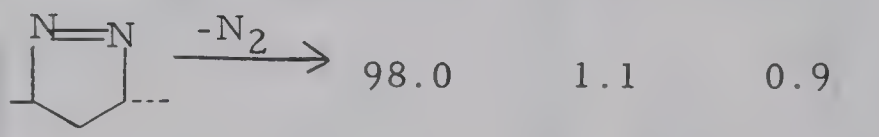
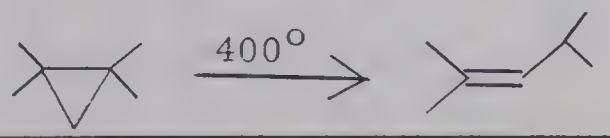
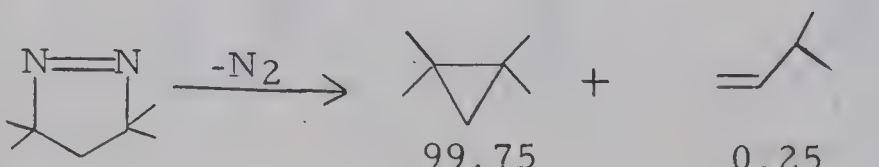
(II)

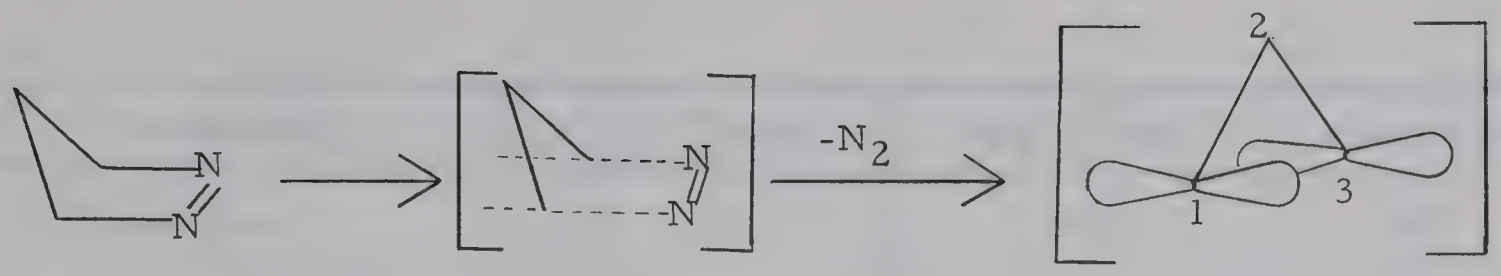
Crawford and Mishra gave the interesting comparisons between the product distributions of the isomerization of cyclo-propane and the thermal decomposition of 1-pyrazolines in Table II.

We are now in a situation that requires explanation of the main factors that determine the stereospecificity of the products arising from the previous precesses. A good deal of such study has been made by Crawford and Mishra. They concluded that there is a folding of the pyrazoline ring to accommodate the insipient sp^2 hybridization of the C_3 and C_5 centers which will in effect have the two developing p-orbitals parallel to each other. Thus they expected that the plane of $C_3C_4C_5$ be almost perpendicular to that of C_3C_5NN.

TABLE II

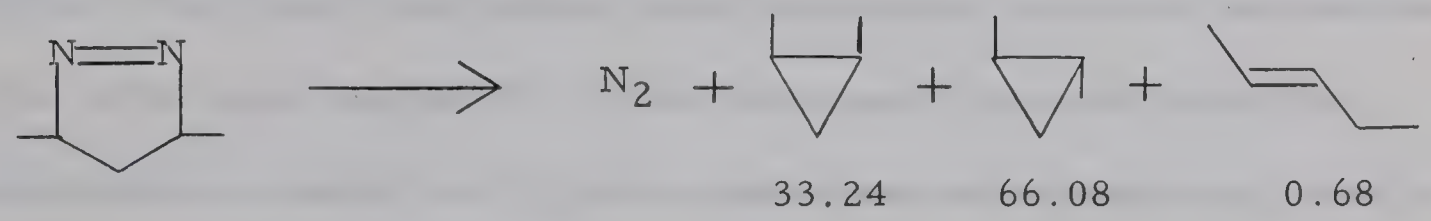
Product Distributions

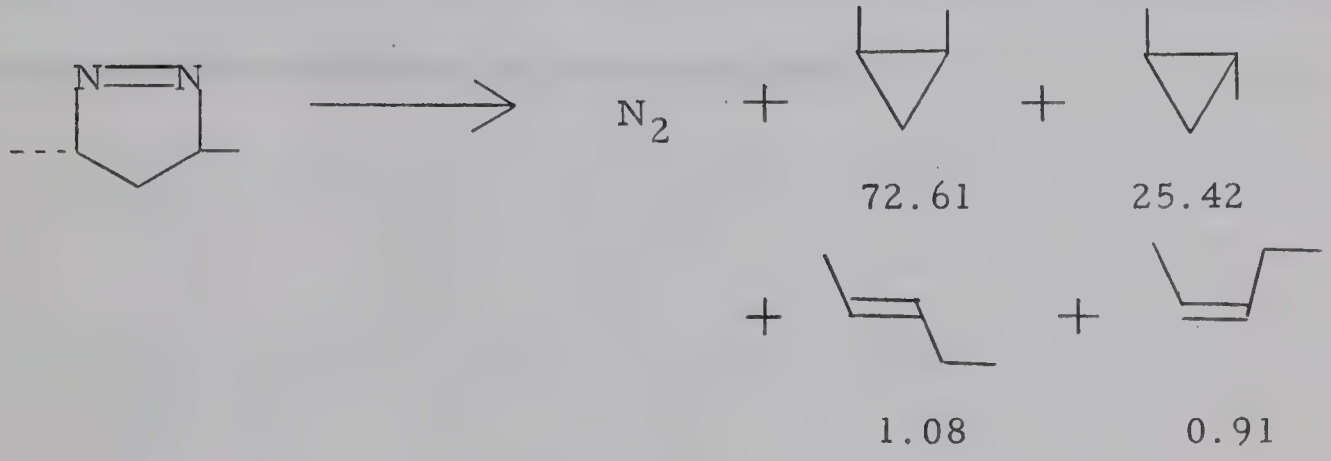
Isomerization of Cyclopropane	Ref.	Thermal Decomposition of 1-Pyrazolines	Ref.
	17		26
	7		26
	17		26
	6a		26
	18		26
	19a		26



(Ts) (1n)

The thermolysis of cis- and trans-3,5-dimethyl-1-pyrazoline gave the following:





As both conrotation and disrotation are allowed on symmetry considerations of initial and final states in the cyclopropane forming step, it is obvious that conrotation is favoured over disrotation in the above example.

Further support given by Crawford and Mishra that the transition state resembles the one suggested, is the kinetic data in Table III.

TABLE III

Compound	Temp.	$k \times 10^4 sec^{-1}$	Relative Rate
1-Pyrazoline	223.0	16.0	1.00
4-Methyl-1-pyrazoline	223.0	15.5	0.97
4,4-Dimethyl-1-pyrazoline	223.0	0.126	0.0079

4,4-Dimethyl-1-pyrazoline decomposes at 1/130 of the rate of 1-pyrazoline, even though one methyl group introduced into the 4-position has little effect upon the rate. The introduction of the second methyl group places a methyl on C_4 on the same side as the departing nitrogen in the transition state. Thus the reaction rate is decreased by making the desired transition state less available.

CHAPTER 2

DEFINITION OF THE PROBLEM

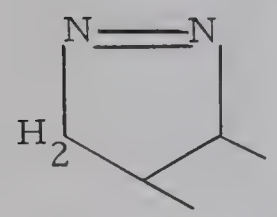
The formation of a singlet trimethylene species as a detectable intermediate in the thermolysis of 1-pyrazolines suggests that these same species may be involved in the addition of singlet methylene to olefins. Skell's hypothesis states that singlet methylene addition to olefins is stereospecific, and that the two new carbon-carbon bonds are formed simultaneously. We have undertaken the problem of determining whether or not the substituted trimethylene species generated by the thermolysis of cis- and trans-3,4-dimethyl-1-pyrazoline are capable of a stereospecific ring closure, and are capable of existence as entities in the addition of singlet methylene to olefins. This requires an assessment of the geometry of the intermediate species produced as well as the products and the starting materials.

CHAPTER 3

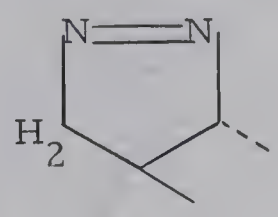
RESULTS AND DISCUSSION

A. Synthesis and Structure of the Pyrazolines

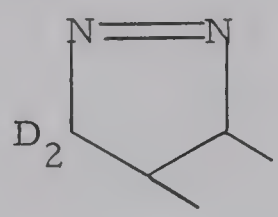
For this work, four different 1-pyrazolines were synthesized:



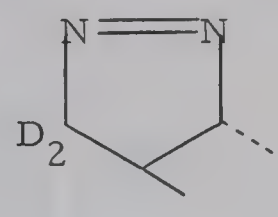
(I)



(II)



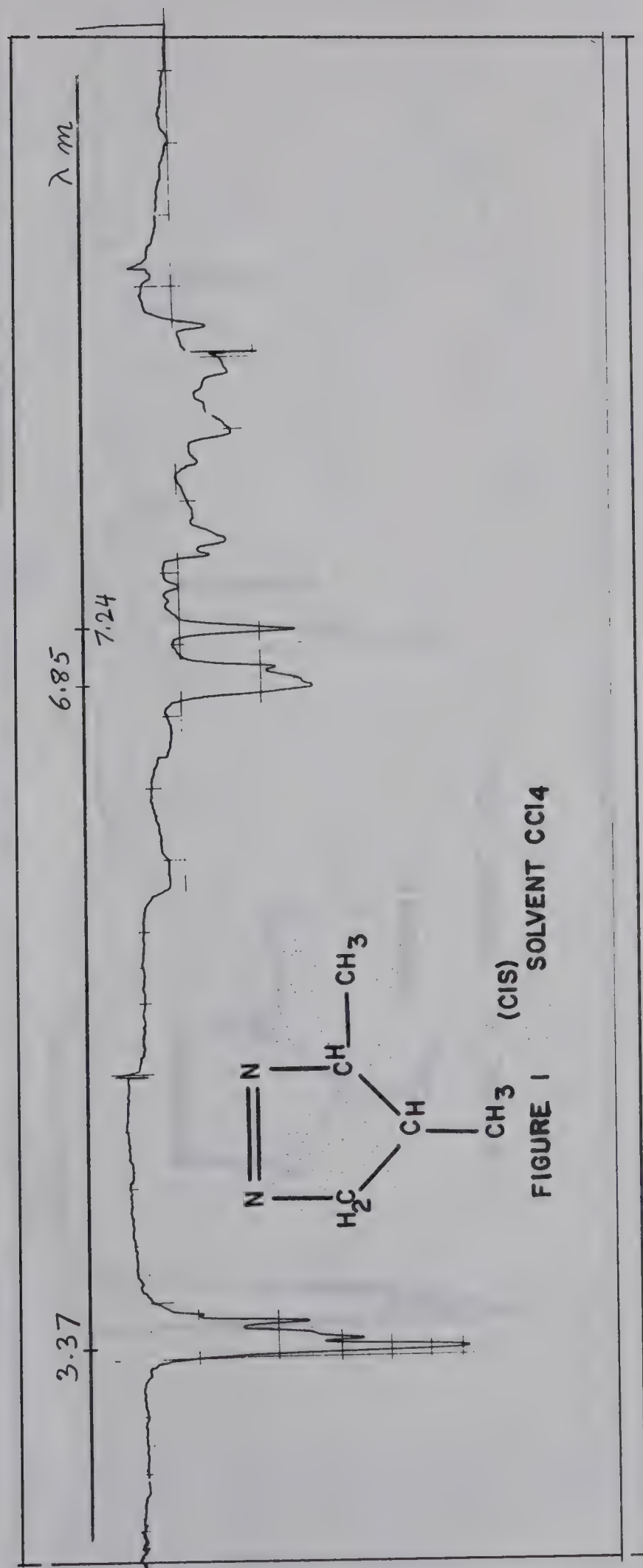
(I-d_2)



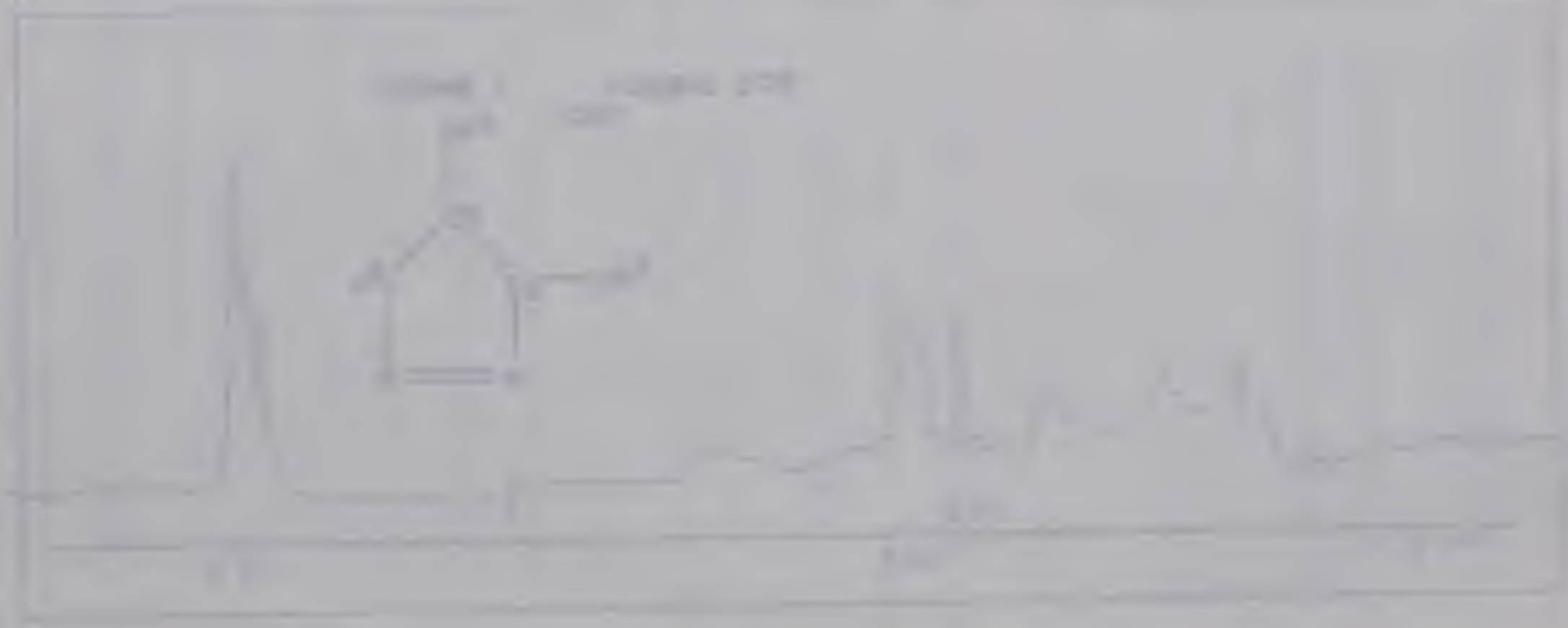
(II-d_2)

The addition of diazomethane to simple olefins has been reported to give pyrazolines[20]. Compounds (I) and (II) were obtained by the addition of an ethereal solution of diazomethane to cis- and trans-2-butene respectively. Compounds I-d_2 and II-d_2 were obtained by the addition of an ethereal solution of dideuteriodiazomethane to the same olefins.

The infrared spectra of I and II are given in Figures 1 and 2 respectively. The presence of the azo group is indicated by the absorption ν_{max} at 1545 cm^{-1}. The ultraviolet spectra of I and II are shown in Figure 3. The absorption at 3233 $\mathring{A}$ in methanol indicates the azo chromophore. The high resolution mass spectrum of compound I, Figure 4, gave 98.0848 as the molecular weight of $C_5H_{10}N_2$ (calculated: 98.0844). The nmr of compounds I, II, I-d_2 and II-d_2 in carbon tetrachloride are given in Figures 5, 6, 7, and 8. The chemical



Infrared Spectrum of cis-3,4-Dimethyl-1-pyrazoline.



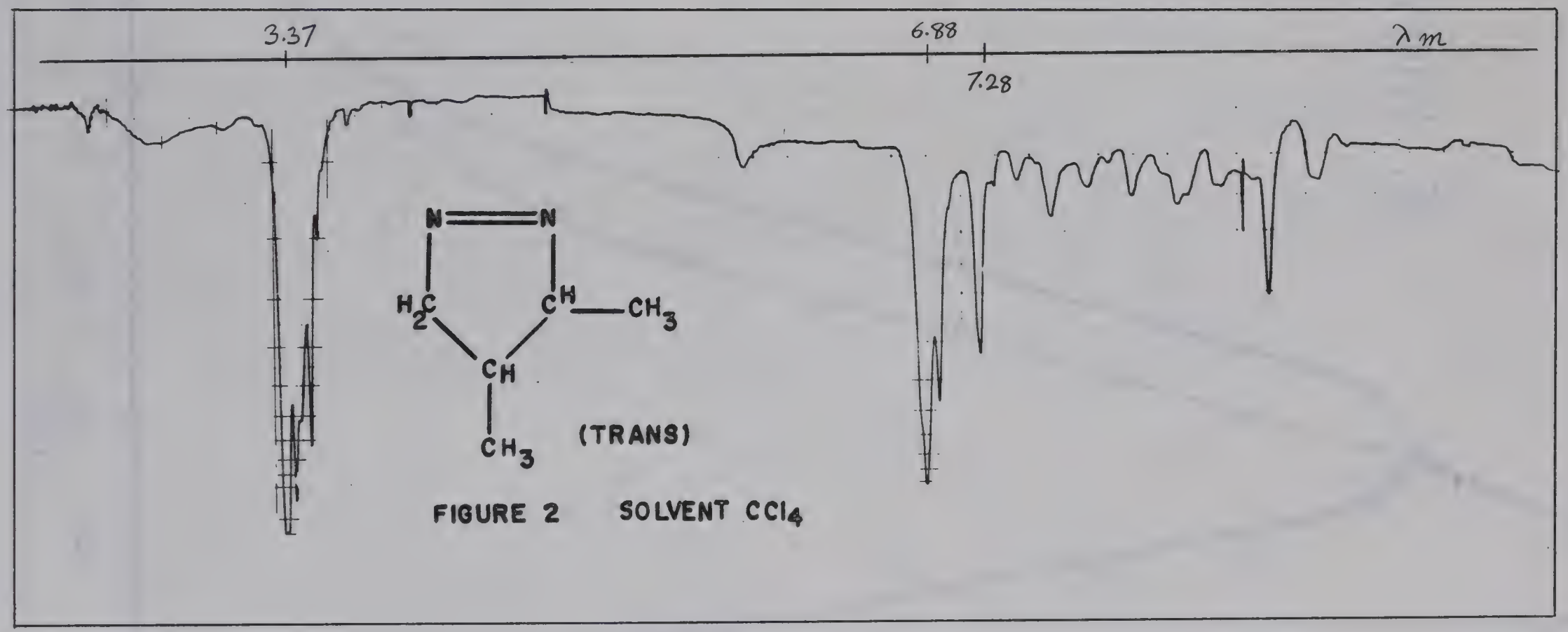


FIGURE 2 SOLVENT CCl_4

Infrared Spectrum of trans-3,4-Dimethyl-1-pyrazoline.

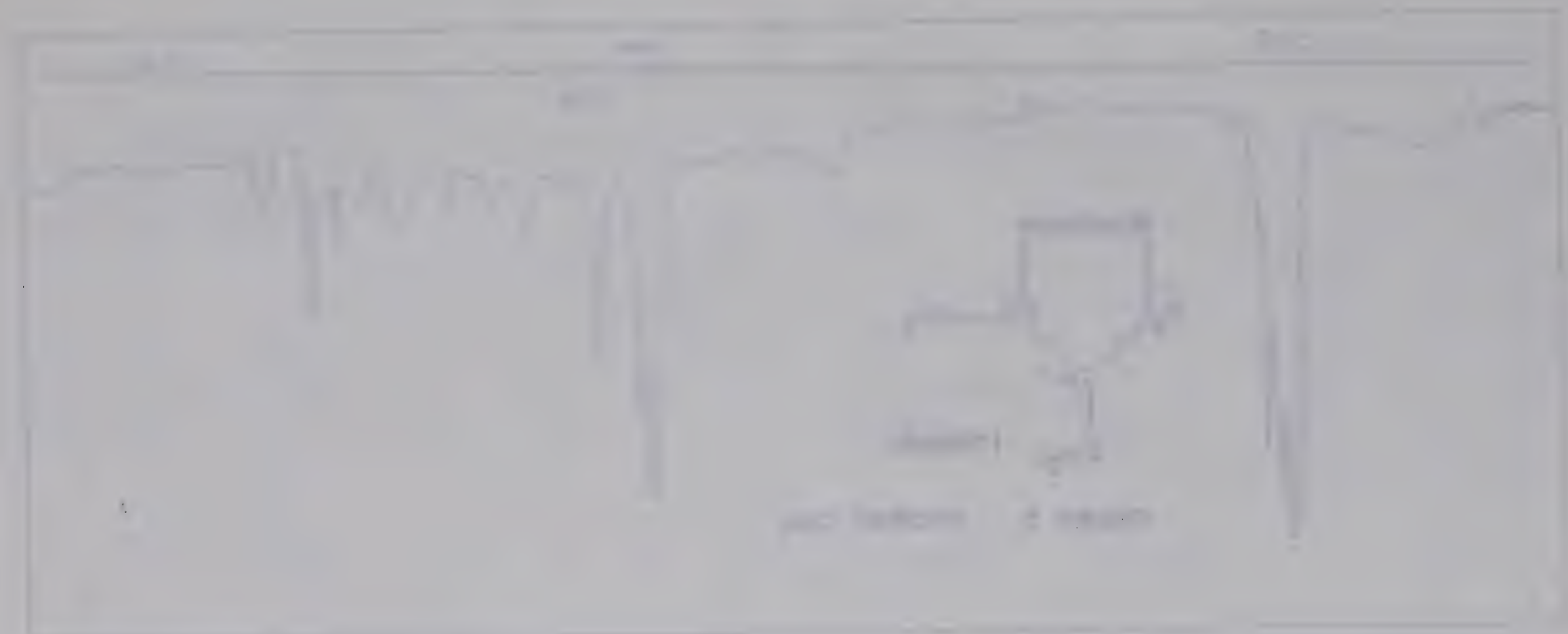
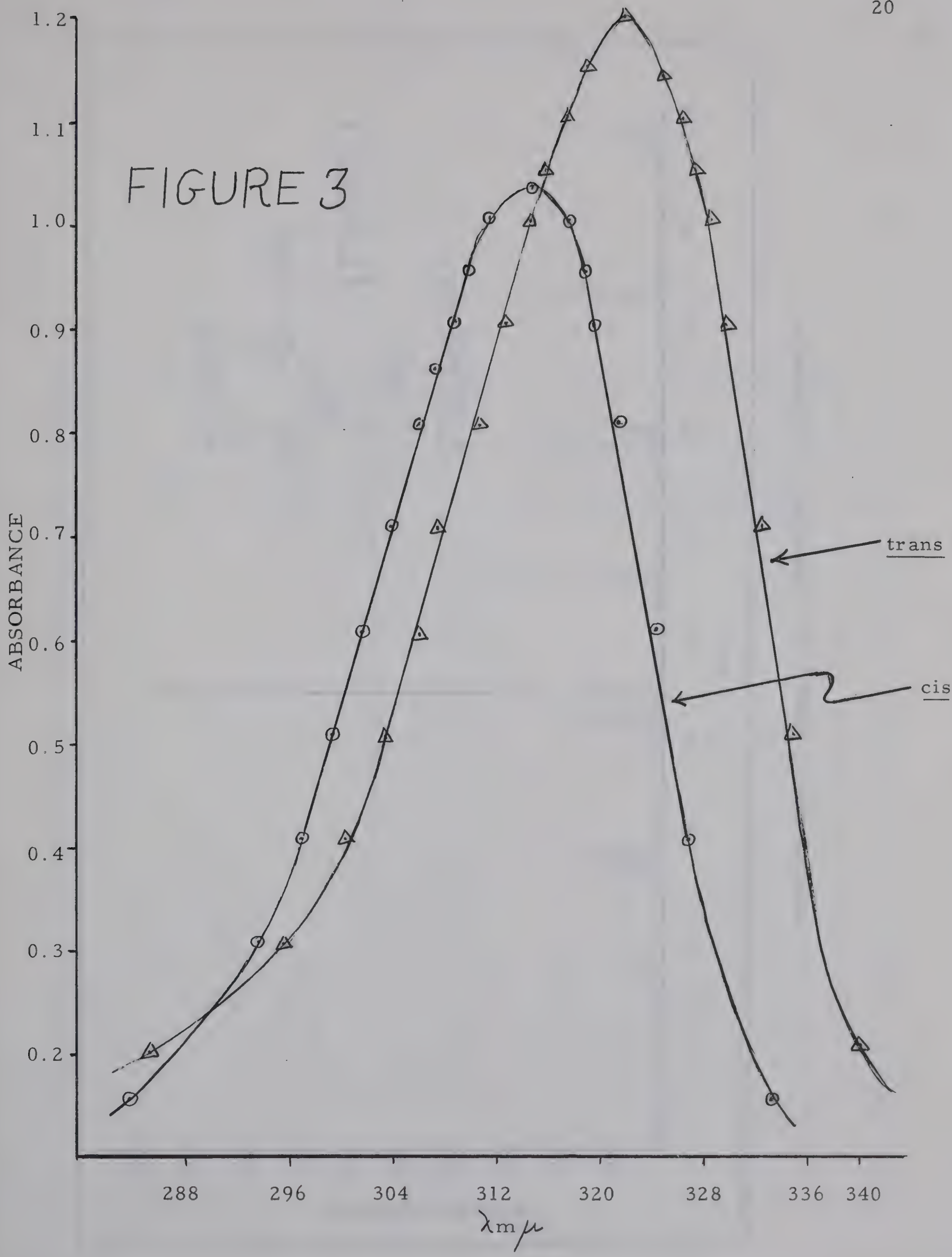
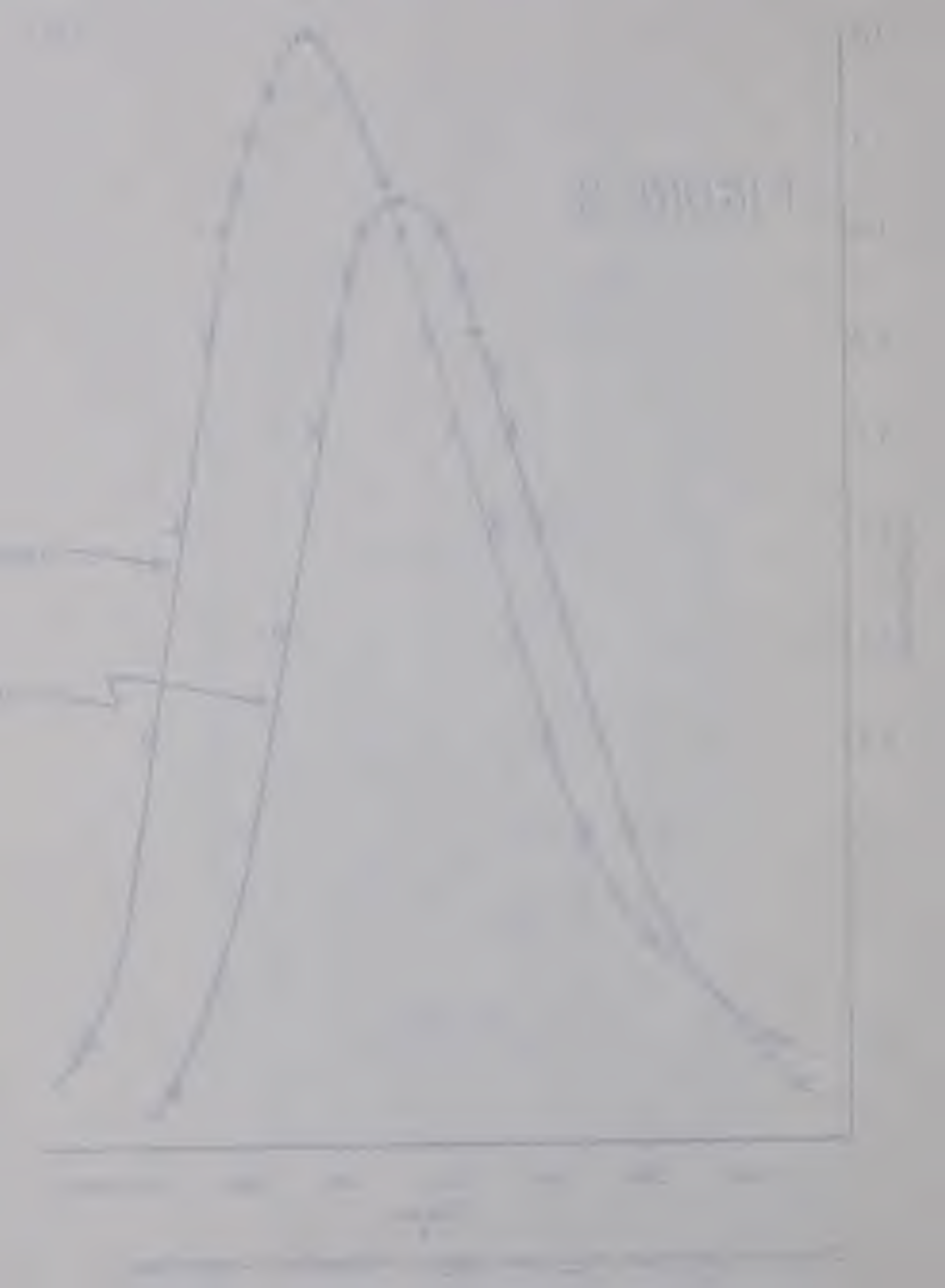
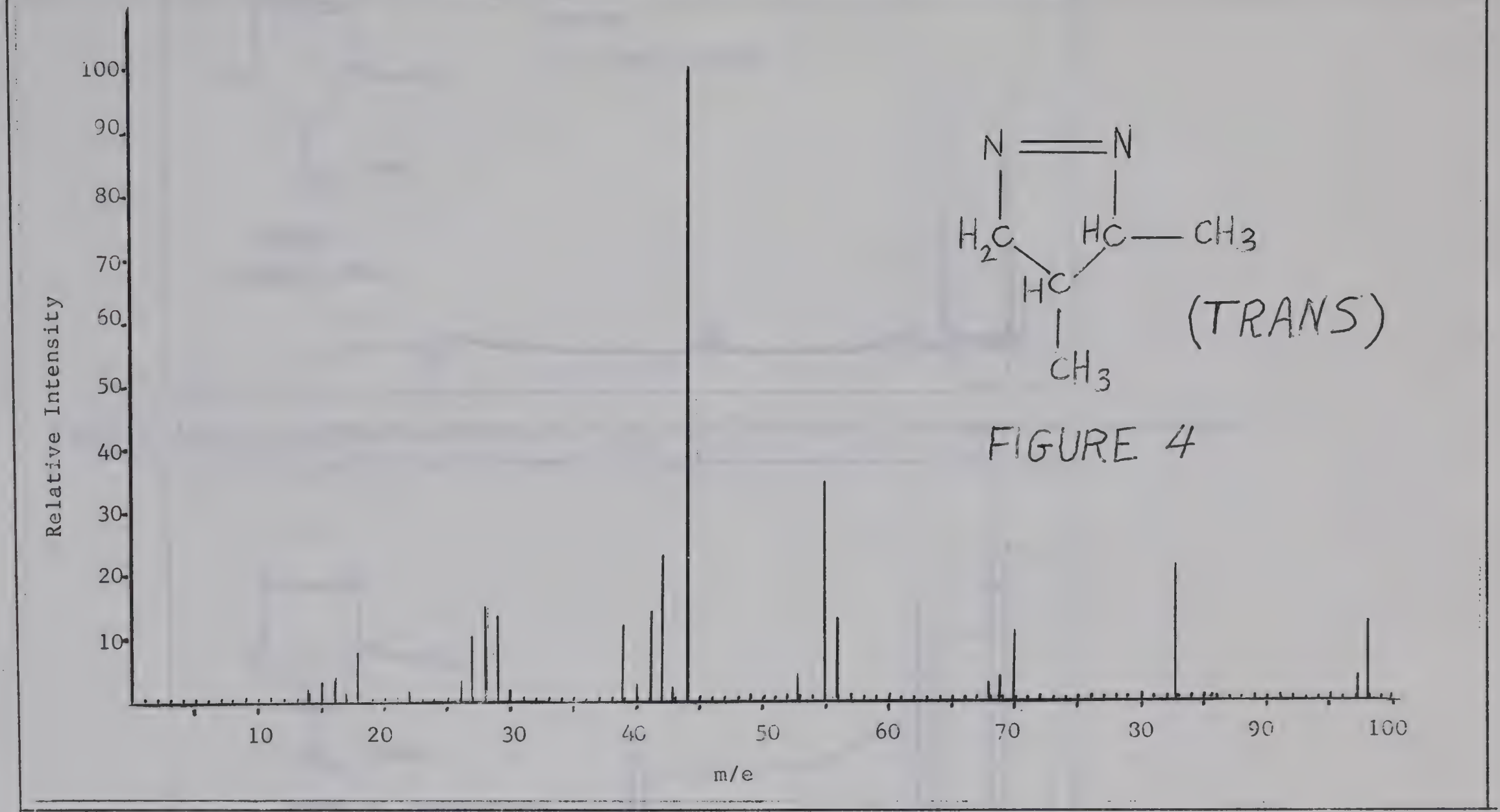


FIGURE 3



Ultraviolet Spectrum of cis- and trans-3,4-Dimethyl-1-pyrazoline.

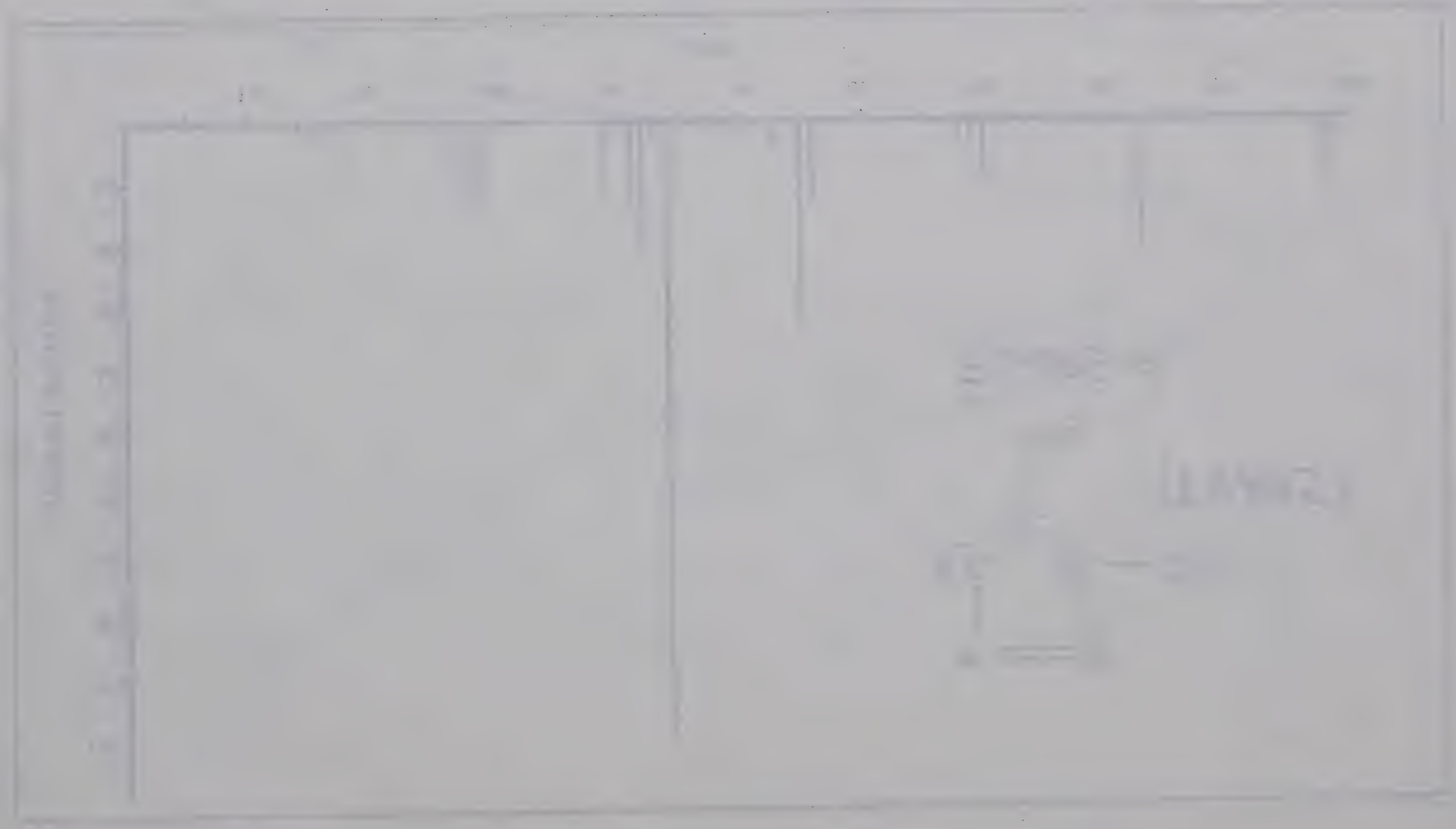


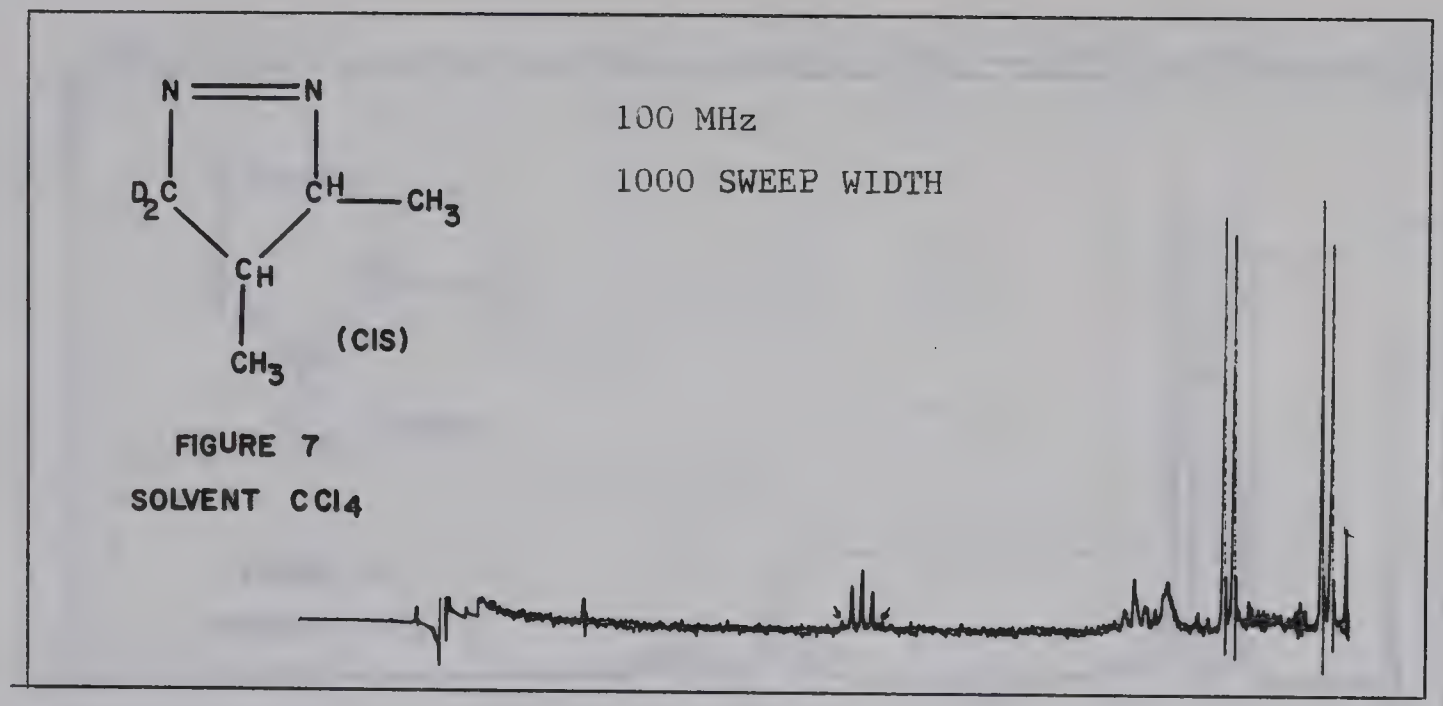


(TRANS)

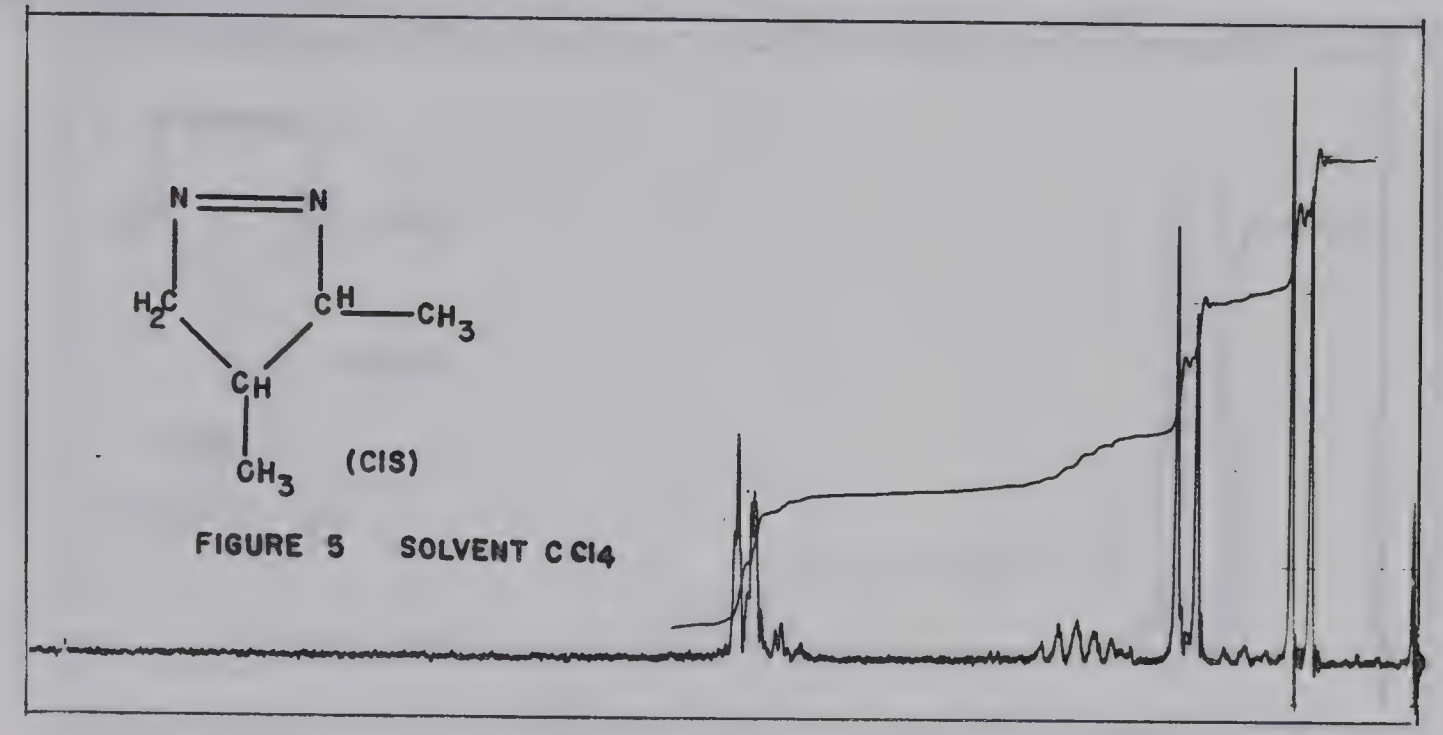
FIGURE 4

Mass Spectrum of <u>trans</u> - 3,4 - Dimethyl - 1 - Pyrazoline

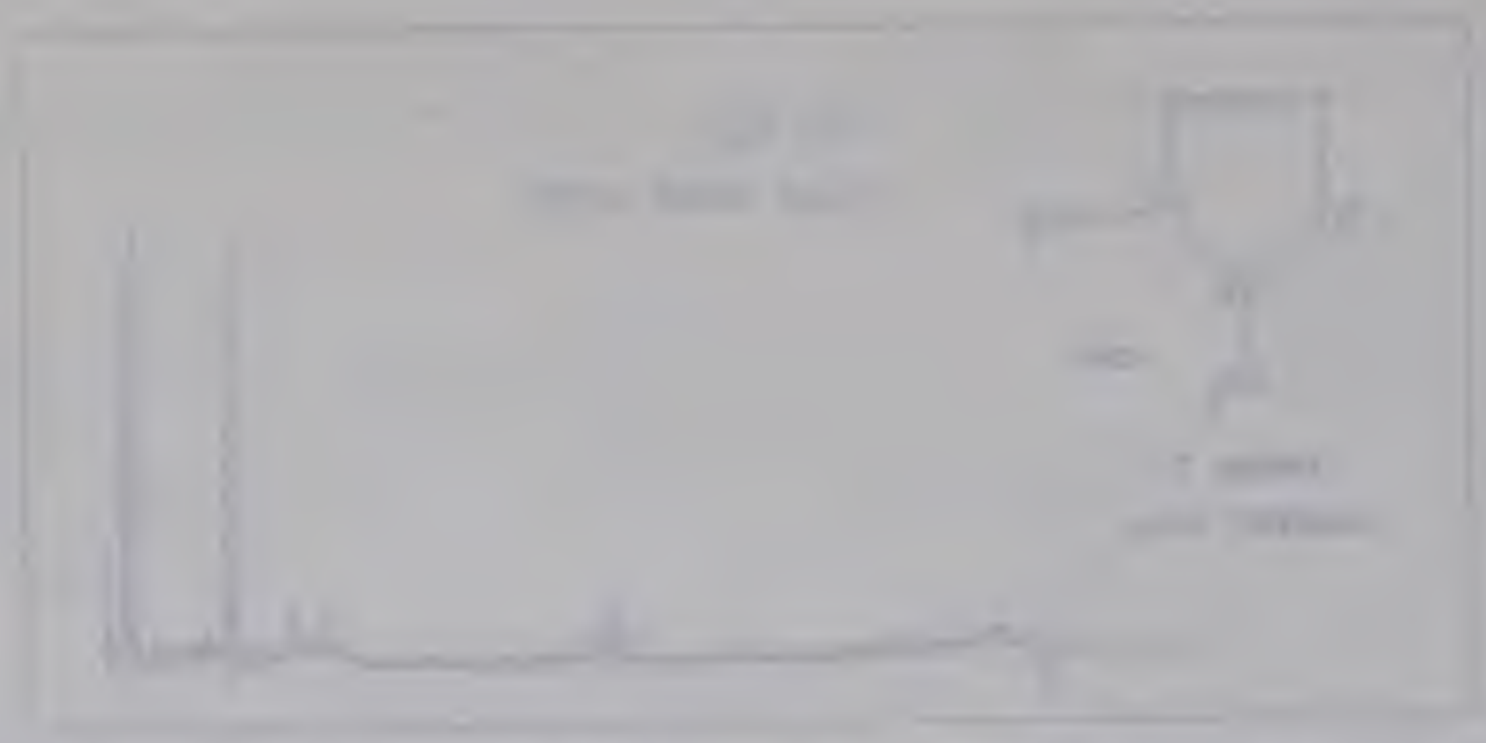


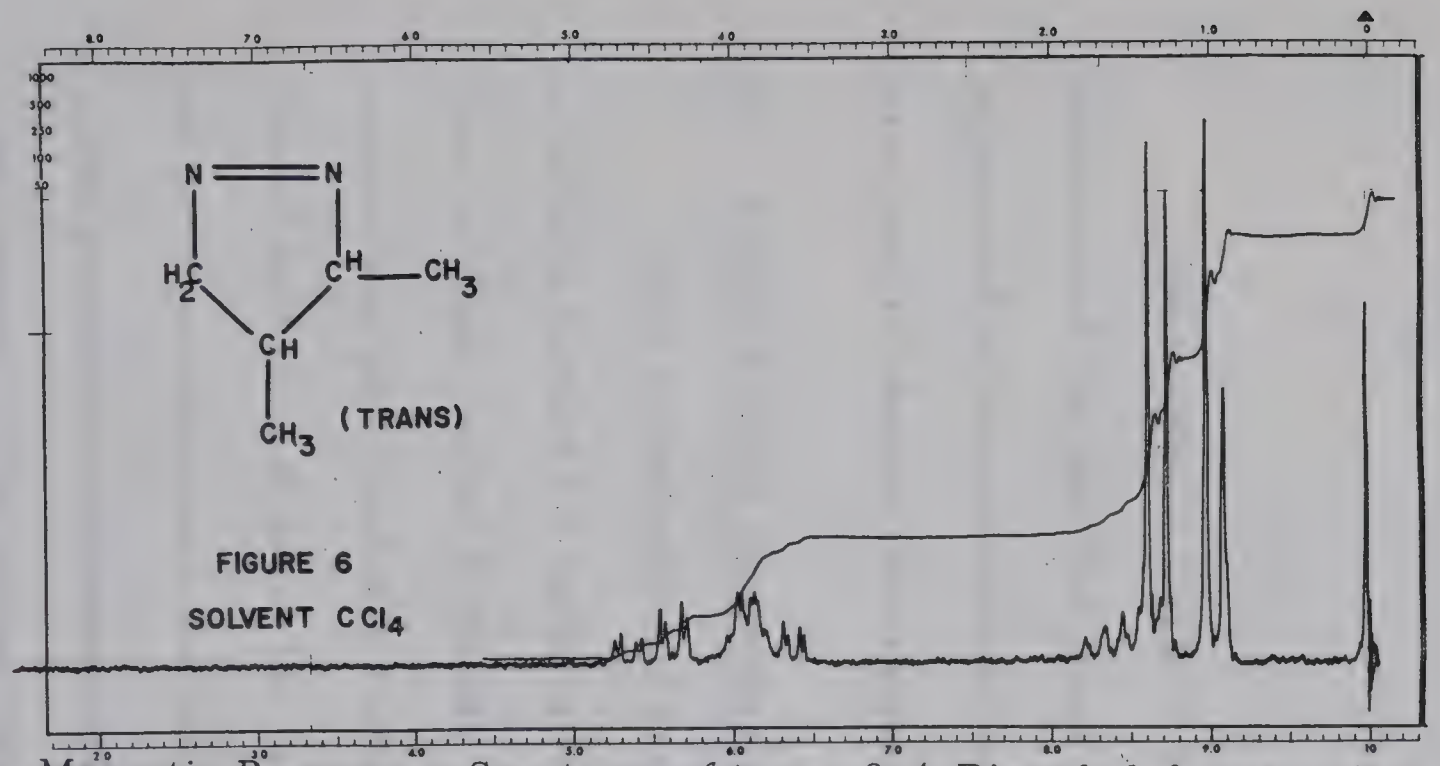


Nuclear Magnetic Resonance Spectrum of cis-3,4-Dimethyl-5,5-dideuterio-1-pyrazoline.

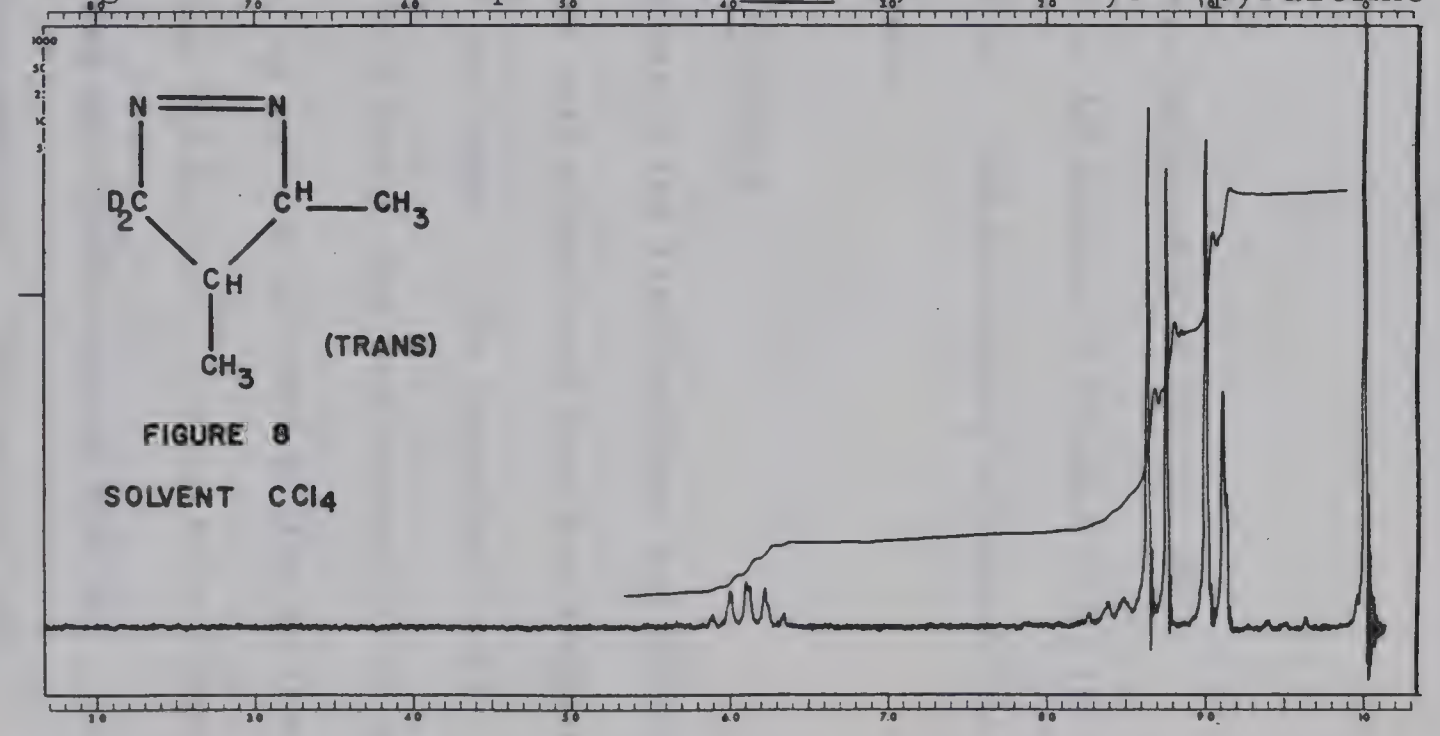


Nuclear Magnetic Resonance Spectrum of cis-3,4-Dimethyl-1-pyrazoline.



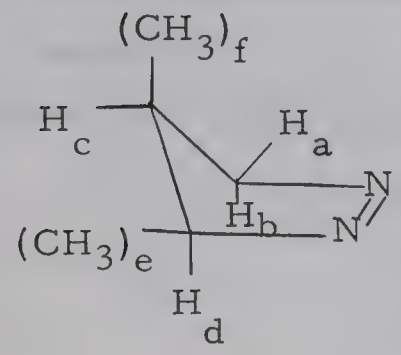


Nuclear Magnetic Resonance Spectrum of trans-3,4-Dimethyl-1-pyrazoline

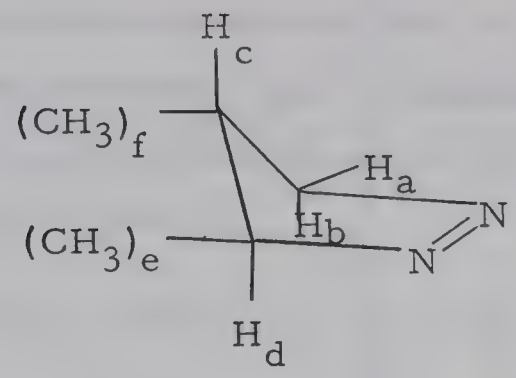


Nuclear Magnetic Resonance Spectrum of trans-3,4-Dimethyl-5,5-dideuterio-1-pyrazoline.

shifts and the coupling constants of all the protons of I and II are given in Table IV.



I



II

The results in Table IV were assigned from the 100 MHz spectrum of I-d_2 and II-d_2 where the AB pattern of protons in C_5 is eliminated by deuterium substitution. The decoupling technique was also used to confirm the assignments.

B. Analysis of the Thermolysis Products

Since all thermolysis products of the 1-pyrazolines are volatile, a suitable method for handling them with a minimum loss was required, thus the bulb crusher technique [21] was used. The compound to be studied was pyrolyzed in a small bulb which then was broken inside a heated port through which the carrier gas was allowed to flow so that all of the products were carried into the detector. Four microliters of the pyrazoline to be examined was put inside a pyrex bulb of approximately 0.2 to 0.4 milliliters capacity. The sample was completely degassed using a high vacuum system by alternate freezing

TABLE IV

Coupling constants and chemical shifts of I and II.

Compound	Coupling Constant, cps	Chemical Shifts, τ
I	$J_{ab} = 16.8$	
	$J_{ac} = 4.7$	$H_a = 5.83$
	$J_{ad} = 2.2$	$H_b = 5.89$
	$J_{bc} = 6.5$	$H_c = 7.91$
	$J_{bd} = 2.2$	$H_d = 5.96$
	$J_{cd} = 7.5$	$(CH_3)_e = 8.58$
	$J_{cf} = 7.0$	$(CH_3)_f = 9.27$
	$J_{de} = 7.5$	
II	$J_{ab} = 16.5$	
	$J_{ac} = 8.0$	$H_a = 5.47$
	$J_{ad} = 2.0$	$H_b = 6.25$
	$J_{bc} = 6.6$	$H_c = 8.50$
	$J_{cf} = 6.5$	$H_d = 6.15$
	$J_{de} = 8.5$	$(CH_3)_e = 8.67$
	$J_{cd} = 8.1$	$(CH_3)_f = 9.03$

Note: J_{ab} related to an AB system.

and melting, and then subsequently sealed. The sealed bulb was then suspended inside the vapour of a refluxing liquid until the thermolysis was completed.

Four different columns (or combinations of columns) were used for the analysis of the thermolysis products:

Column A: 8 meters of 23% 2,5-hexanedione + 2 meters silver nitrate-saturated propylene glycol on fluoropak.

Column B: 24 ft silver nitrate-saturated propylene glycol on firebrick.

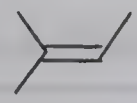
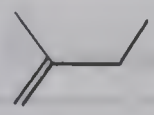
Column C: 10 ft 20% dimethyl sulfolane (DMS) on fluoropak.

Column D: 10 ft 20% DMS + Column B

Because the best resolution of g.c. peaks was obtained on column D, the results of thermolysis analyzed using that combination of columns are reported. Table V shows the products and their percentages of the thermolysis of the pyrazolines I and II. The differences in the percentages of each component on columns A, B and C, and with the more reliable results on column D, are attributed to the poor resolution of the g.c. peaks on the first three columns resulting in errors.

TABLE V

Analysis of the Thermolysis products

Compound	Column	 %	 %	 %	 %
I	A	43.64	33.00	16.69	6.67
	B	44.10	31.20	17.10	7.30
	C	42.05	34.23	16.86	7.00
	D	45.45 ± 0.1	33.00±0.6	14.37±0.3	7.25±0.4
	D*	43.3 ± 0.3	35.2 ± 0.3	14.4 ± 0.2	7.2 ± 0.2
II	A	45.22	22.67	15.88	16.22
	B	47.20	21.80	15.40	16.30
	C	43.32	20.36	20.23	16.48
	D	46.0 ± 0.5	21.8 ± 0.3	16.3 ± 0.3	15.8 ± 0.2

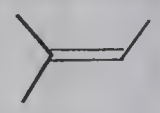
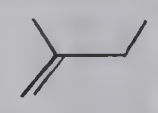
D* R. Moore using a break seal method.

Table VI shows the conditions and the retention times of the products on the four columns.

The thermolysis temperature did not have any appreciable effect on the product composition. This was confirmed when samples were pyrolyzed in a stainless steel reactor (see kinetic studies) and then analyzed. The temperature range from 210-235°C had no effect.

TABLE VI

Conditions and retention times of the thermolysis products.

Column	Conditions		Retention Times in Minutes			
	Temp. °C	Flow rate cc/min				
A	-6	45	33	51	61	46
B	3	30	2.8	3.6	8.8	21.8
C	10	30	6.1	9.7	11.1	8.9
D	room temp.	60	9.5	12.6	16.8	22.0

Note: Helium was used as the carrier gas.

The extent of thermolysis also had no effect on the product composition. This was confirmed when three samples were pyrolyzed for five, ten and fifteen half-lives. The results were within ±1% when comparing each component from the three runs.

The identification of the thermolysis products was based on:

(a) Comparison of the retention times of the products with those given in the literature[22] for the C_5 hydrocarbons.

(b) Each peak in the g.c. was trapped in a cold trap, and the nmr and IR spectrum of each was obtained.

Figures 9, 10, 11, and 12 show the IR of each product compared with an IR spectrum of the expected authentic sample.

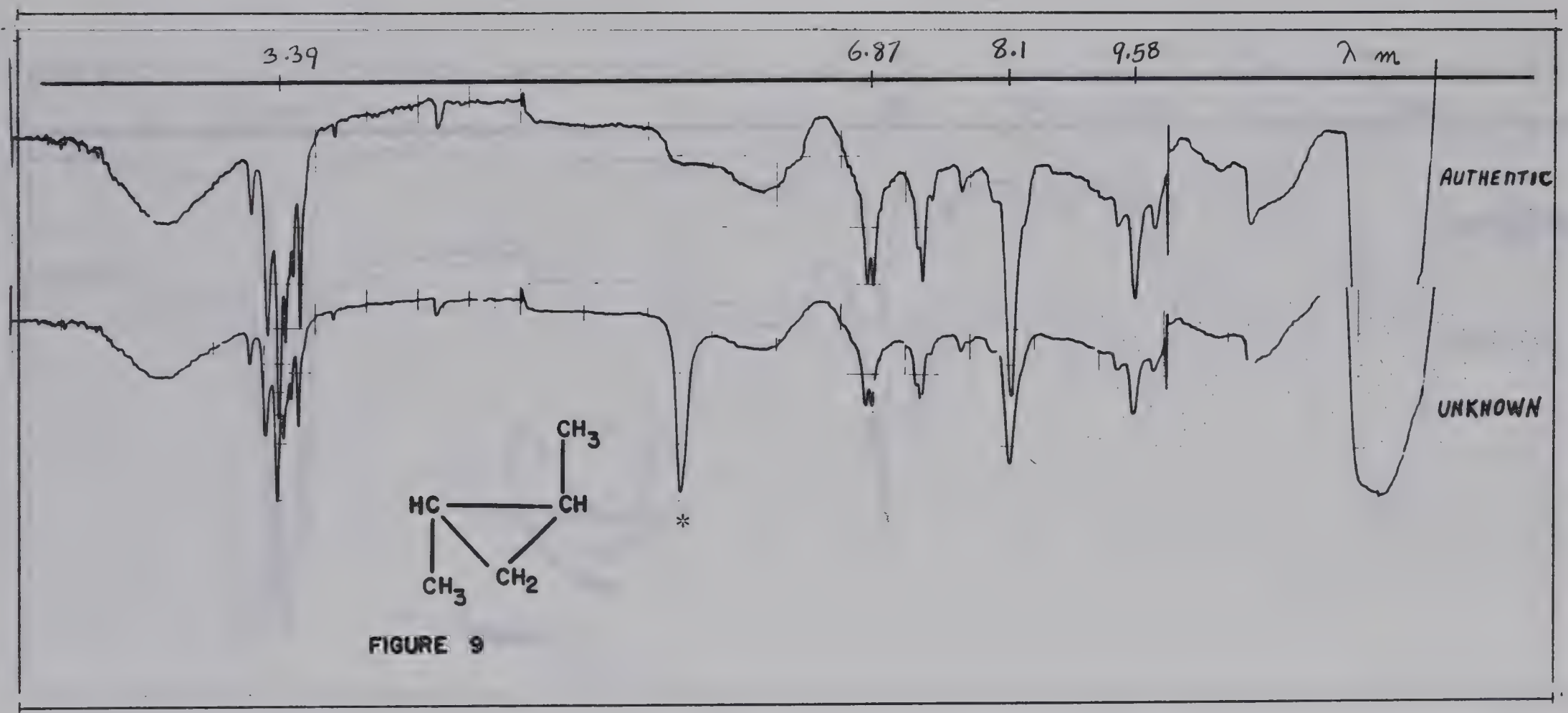
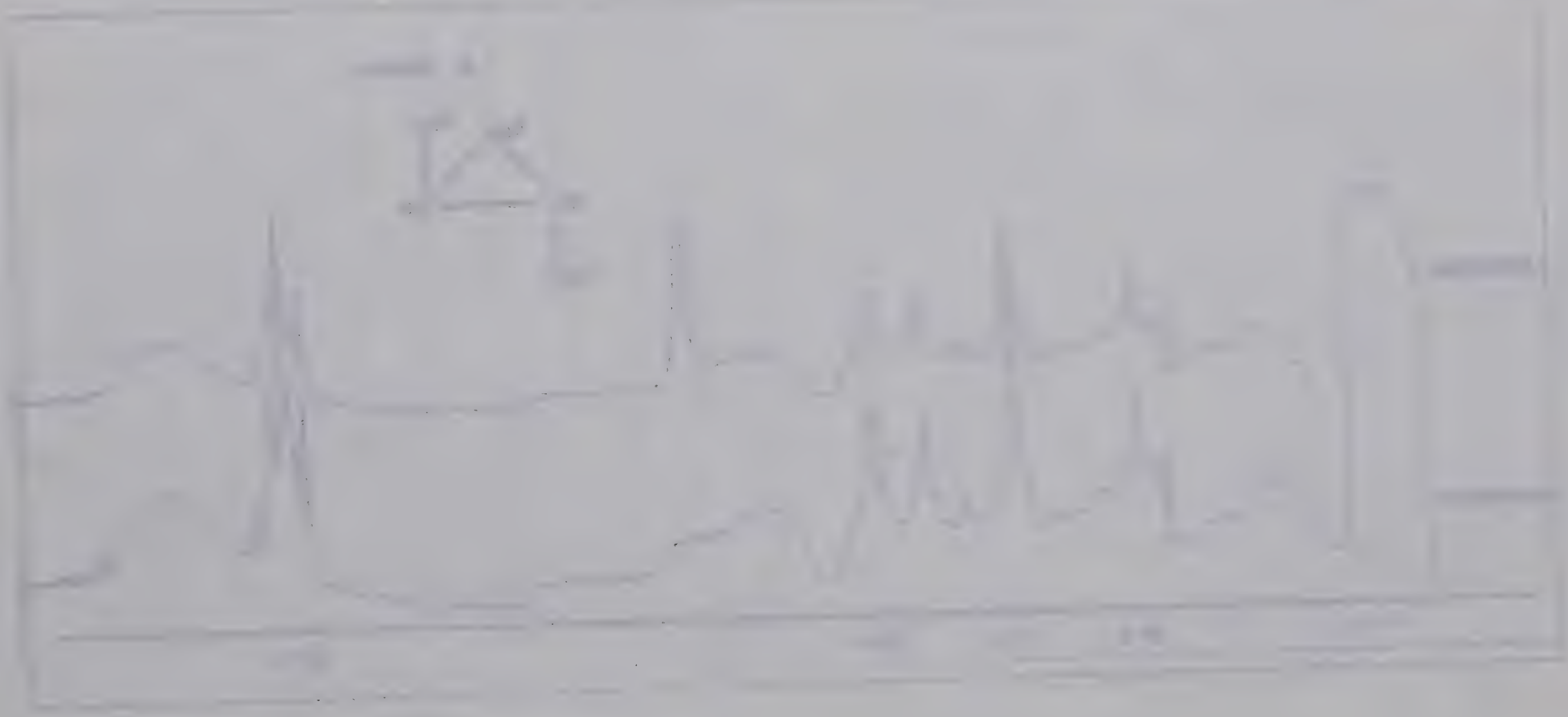


FIGURE 9

Comparison of the Infrared Spectra of trans-Dimethylcyclopropane Obtained from Thermolysis of the Pyrazolines with an Authentic Sample.

The word unknown refers to the component obtained from the thermal decomposition of the 1-pyrazoline.

* The peak 5.73 micron (carbonyl) in the unknown spectrum is coming from the column used in the analysis, namely from 2,5-hexane dione (see column A in the analysis section).



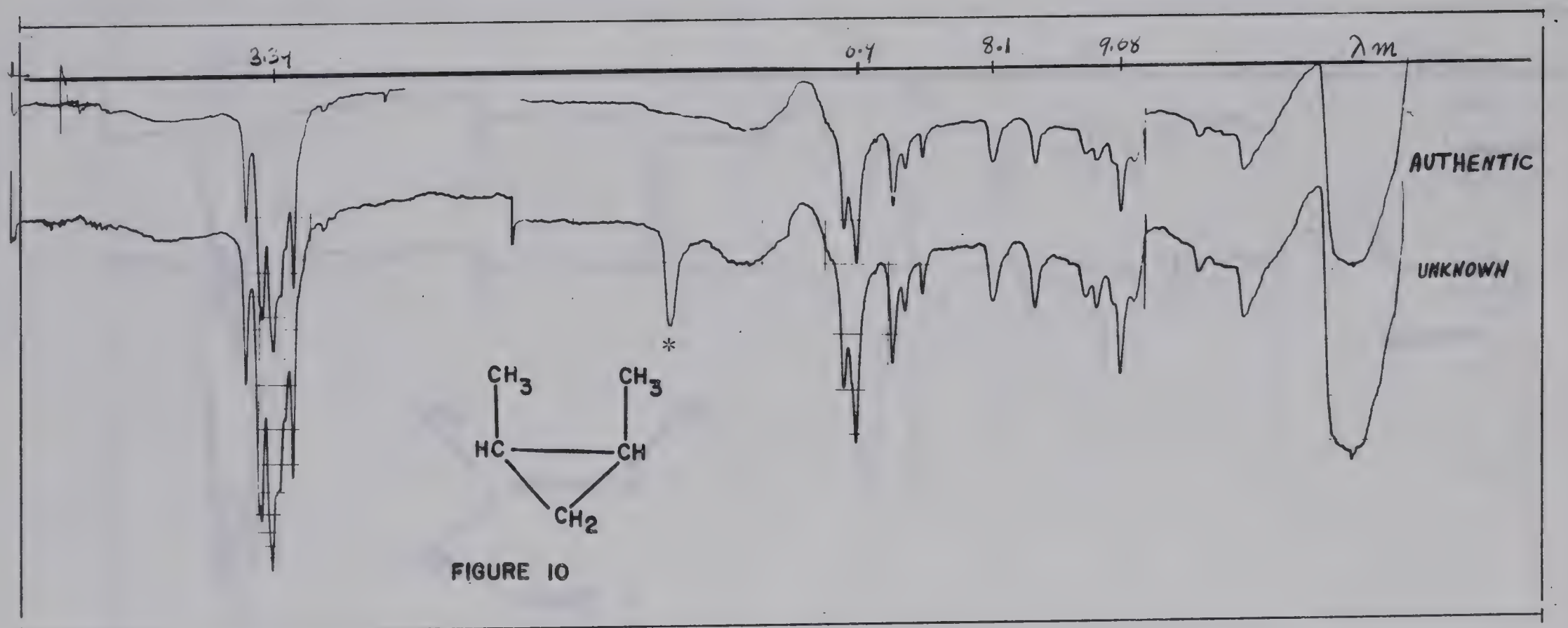
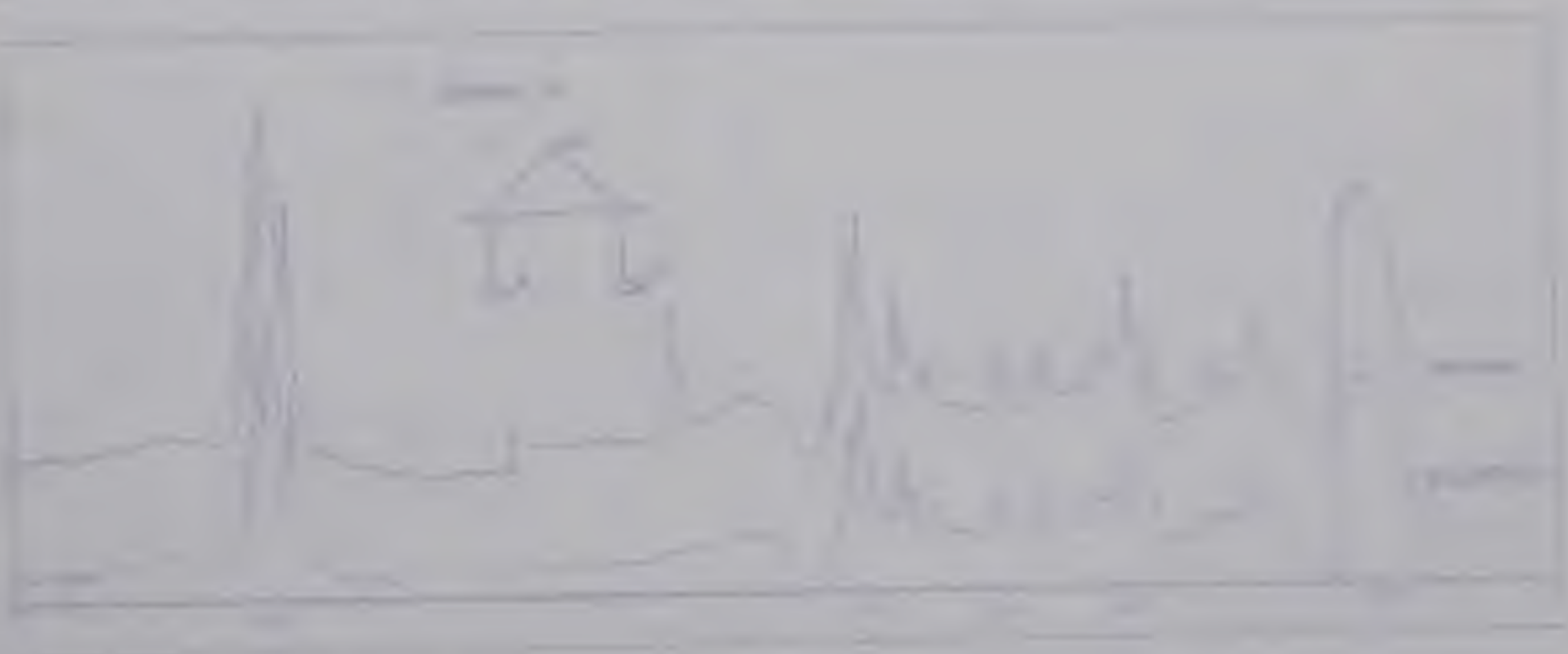


FIGURE 10

Comparison of the Infrared Spectra of cis-Dimethylcyclopropane Obtained from Thermolysis of the Pyrazolines with an Authentic Sample.

The word unknown refers to the component obtained from the thermal decomposition of the 1-pyrazoline.
*The peak 5.73 micron (carbonyl group) in the unknown spectrum is coming from the solumn used in the analysis, namely from 2,5-hexane dione (see column A in the analysis section).



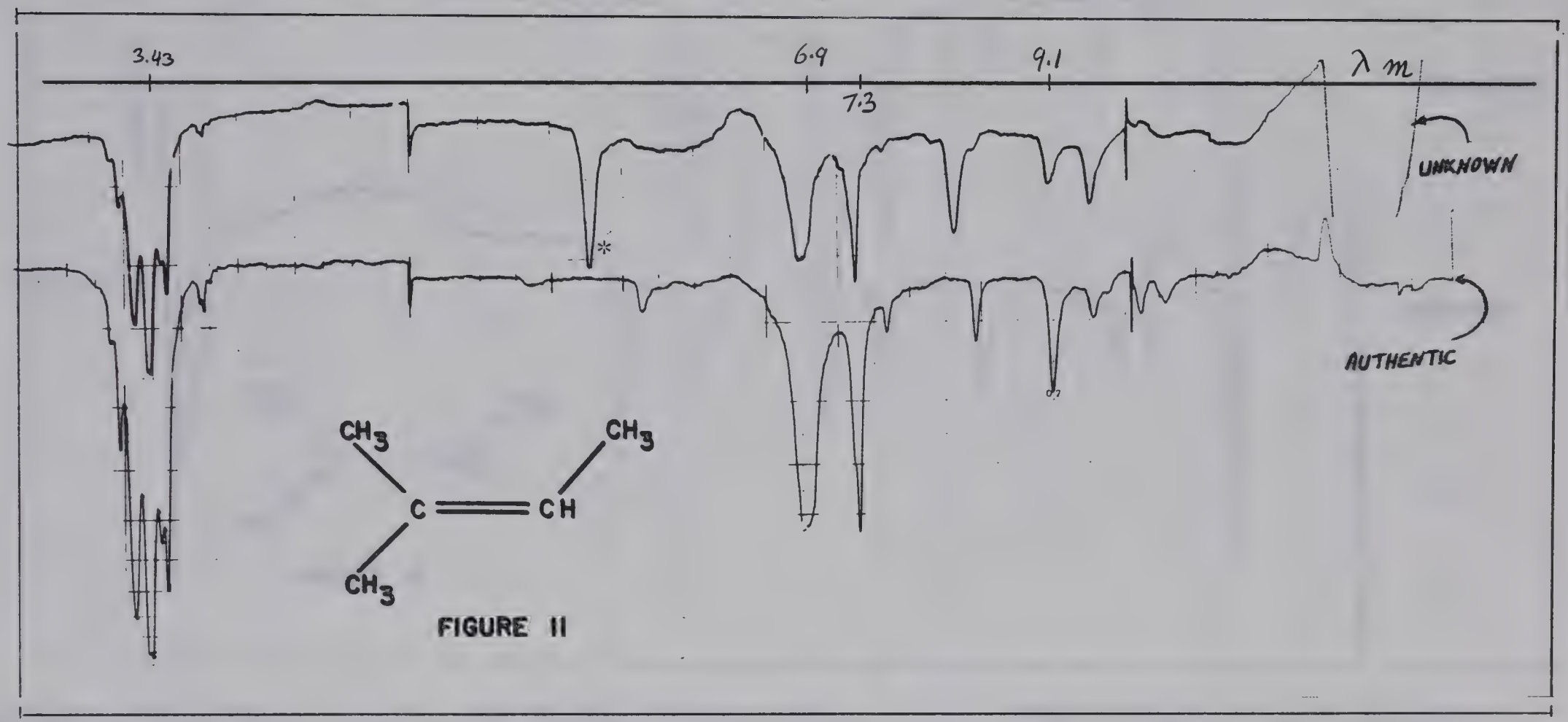
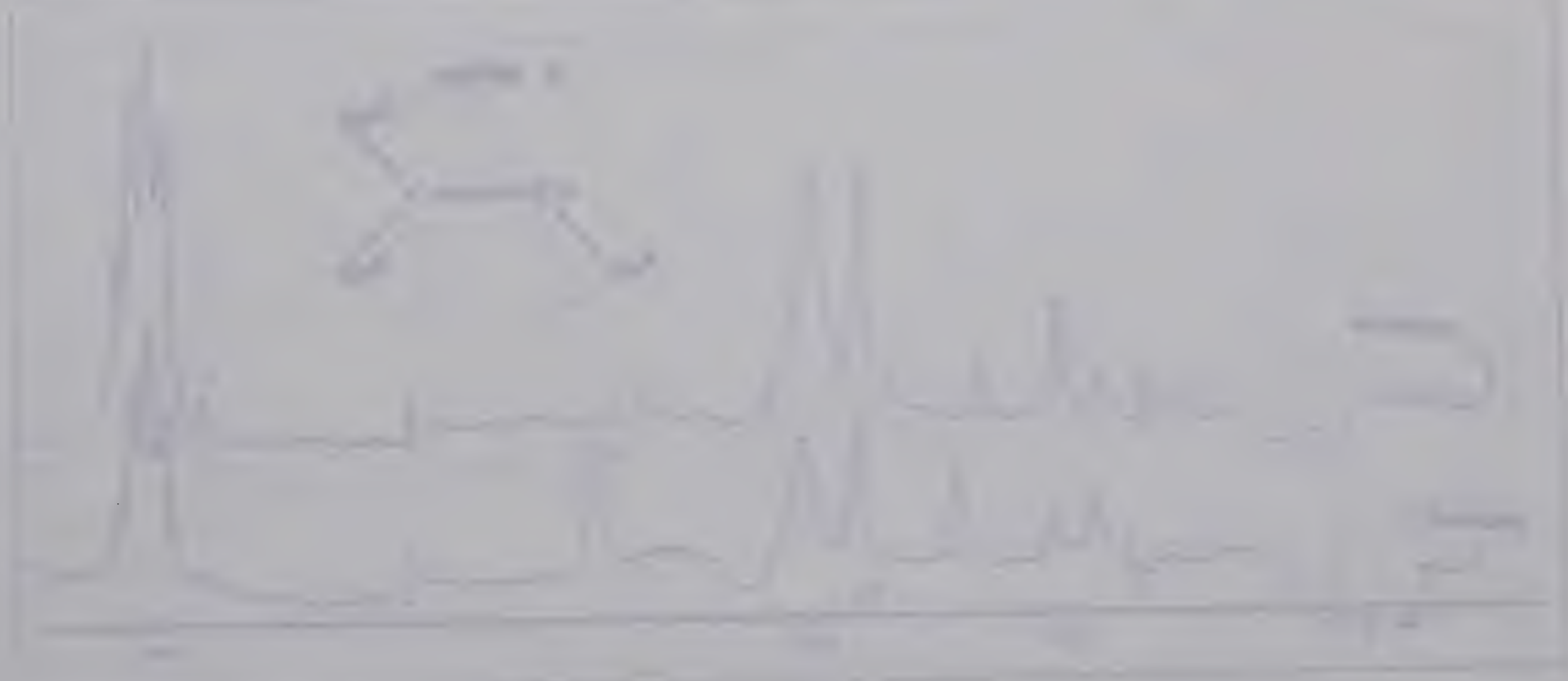


FIGURE II

Comparison of the Infrared Spectra of 2-Methyl-2-butene Obtained from Thermolysis of the Pyrazolines with an Authentic Sample.

The word unknown refers to the component obtained from the thermal decomposition of the 1-pyrazoline.
*The peak 5.73 micron (carbonyl group) in the unknown spectrum is coming from the column used in the analysis, namely from 2,5-hexane dione (see column A in the analysis section).



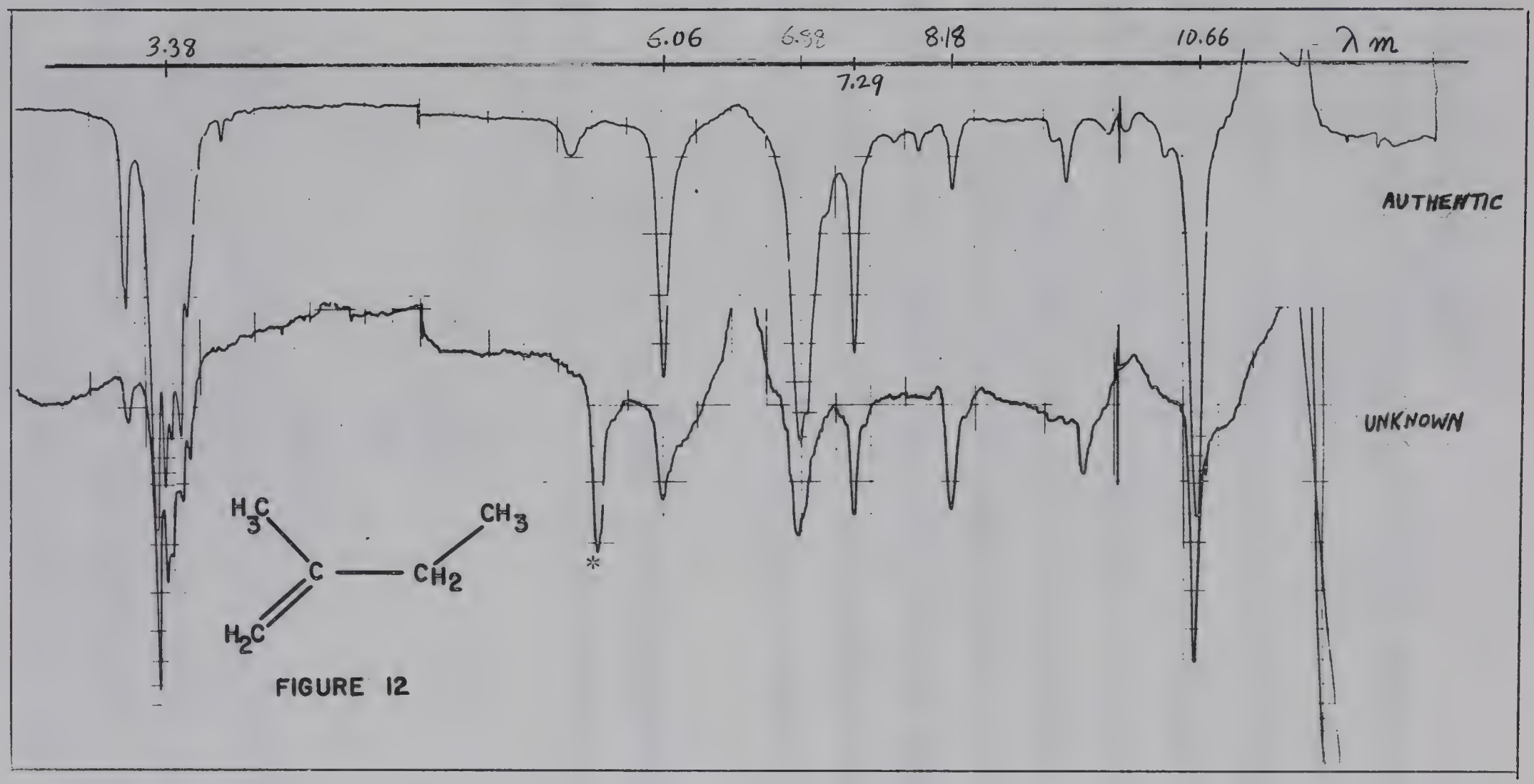
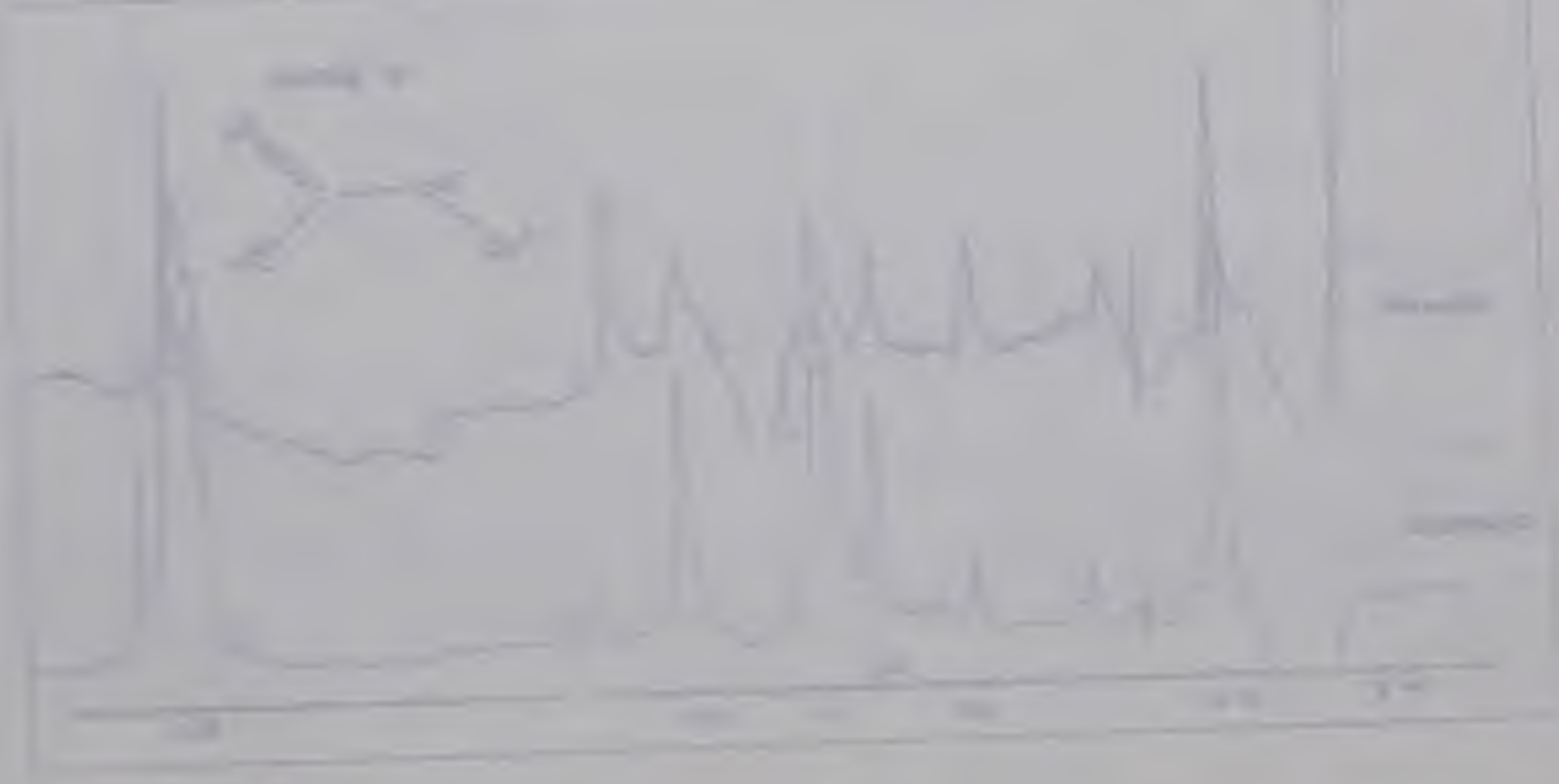


FIGURE 12

Comparison of the Infrared Spectra of 2-Methyl-1-butene Obtained from Thermolysis of the Pyrazolines with an Authentic Sample.

The word unknown refers to the component obtained from the thermal decomposition of the 1-pyrazoline.
*The peak 5.73 micron (carbonyl group) in the unknown spectrum is coming from the column used in the analysis, namely from 2,5-hexane dione (see column A in the analysis section).



C. Kinetic Measurements

Ramsberger[23] and Overberger[24] have studied the kinetics of azomethane and its simple alkylated derivatives. The most convenient way for measuring the rate of decomposition of a compound accompanying a pressure change is to measure the rate of change of pressure in a static system, provided the stoichiometry of the decomposition is known. The aliphatic azo compounds, like our system of 1-pyrazolines, give on thermolysis one mole of nitrogen and one mole of volatile hydrocarbon products, therefore this was the kinetic method chosen for our system. The reactor which was designed by Smith and coworkers[25] in the study of the thermolysis of esters in the gas phase has been used in our study.

An electromotive force (emf) can be generated by mechanical displacement caused by pressure. The relationship is given by the expression:

$$E = ap + b \qquad (1)$$

E = emf

p = pressure

where a and b are constants depending on the geometry of the transducer. The rate of change of E corresponding to the rate of change of p can be continuously recorded on a chart paper moving with a calibrated speed.

For a first order gas phase reaction of the type:

$$A \longrightarrow \text{products}$$

it is known that[26]:

$$k = \frac{2.303}{t} \log \left(\frac{p^a_\infty - p^a_o}{p^a_\infty - p^a_t} \right) \qquad (2)$$

k = the first order rate constant

t = time from the beginning of the reaction when the actual pressure is p^a_t

$$P = p^a - p_x \qquad (3)$$

P = pressure actually observed

p_x = pressure required to push the diaphragm from its normal position to touch the needle

From expressions (1) and (3):

$$E = a(p^a - p_x) = b \qquad (4)$$

or

$$p^a = \frac{E - b}{a} + p_x$$

From (2) and (4):

$$k = \frac{2.303}{t} \log \left(\frac{E_\infty - E_o}{E_\infty - E_t} \right) \qquad (5)$$

Equation (5) can be solved numerically or graphically to give the value of k. E_∞ was taken as the value of E measured after more than seven half lives of the reaction, i.e. more than 99% decomposition[21].

The easiest way to solve the linear equation (5) is by graphical plot of $\log (E_\infty - E_t)$ versus time, so that the slope is given by $-\frac{k}{2.303}$, where k can be readily evaluated.

The activation parameters were obtained from the Arrhenius equation:

$$k = Ae^{-E_a/RT}$$

E_a = activation energy

A = the frequency factor

Equation (6) can be rewritten as:

$$\log k = -E_a/2.303RT + \log A$$

Thus plotting log k versus 1/T give $E_a/2.303R$ as the slope, and log A is the intercept.

Table VII summarizes the kinetic parameters.

TABLE VII

Kinetic data.

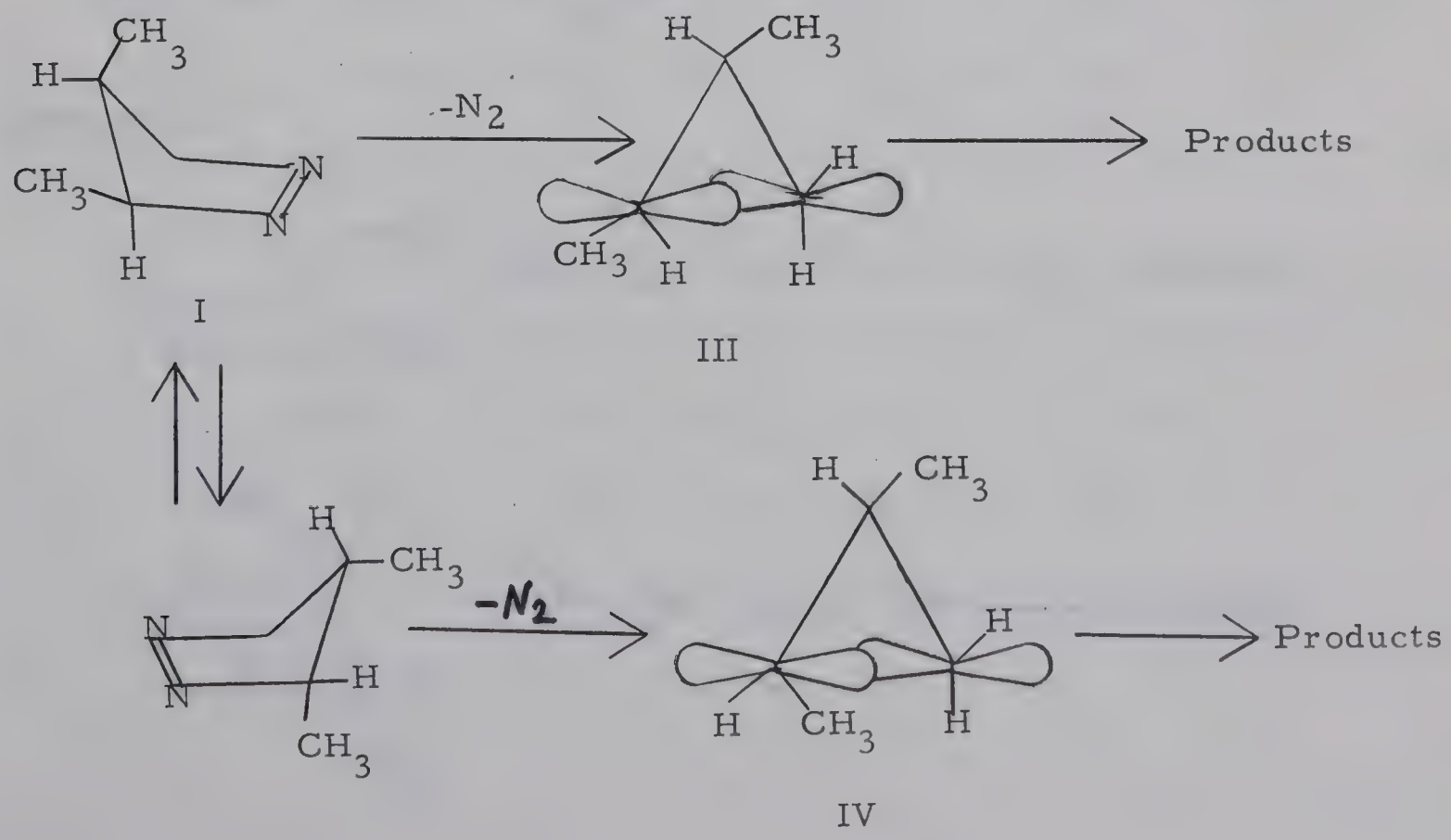
Compound	Temp.[a]	$10^4 \times k$ (sec^{-1})	E_a kcal/mole	log A	$\frac{k_H}{k_D}$
I	210.4 ± 0.1	5.30[a]			
	220.9	12.00	39.0 ± 0.6	14.23 ± 0.5	
	229.8	27.90			
I-d_2	220.9	10.80			1.19 ± 0.05
II	210.4	4.00			
	220.9	9.66	41.6 ± 0.3	15.36 ± 0.5	
	229.8	20.40			
II-d_2	220.9	8.02			1.21 ± 0.05

D. Determination of the Geometry of the Intermediates Involved

The kinetic data of the thermolysis reactions given in Table VII indicates that compounds I and II proceed with activation energies similar to those of previously studied pyrazolines[27, 13]. The secondary kinetic isotope effects observed imply that the primary carbon to nitrogen bond is also breaking in the rate determining step[27b, 28]. The products produced by thermolysis of I and II their proportions are indicated in Table VI.

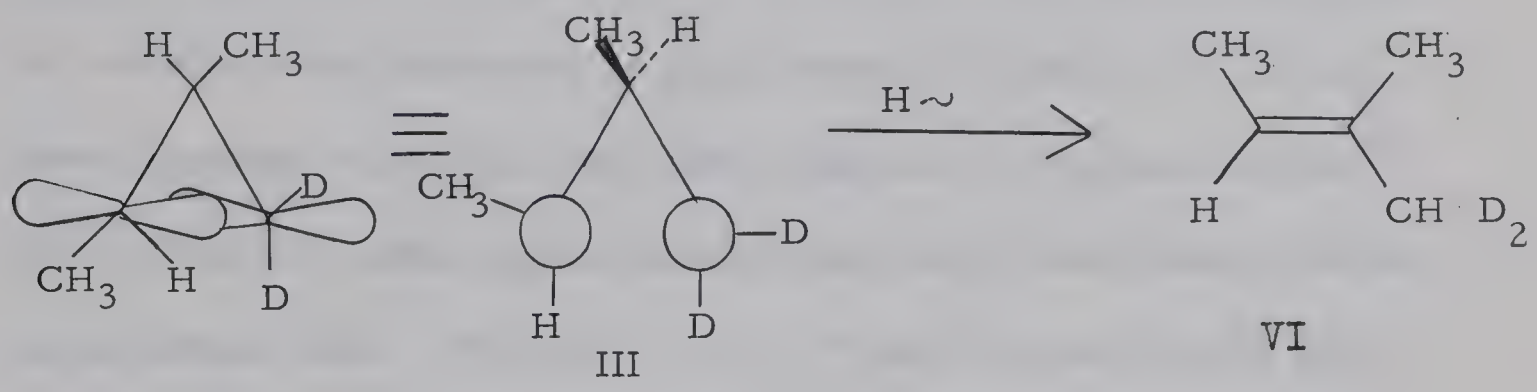
At first glance, Table VI would appear to indicate that the thermolysis is not stereospecific. However, if we consider in detail the nature of the intermediates arising from the thermolysis of I and II, we find that both isomers are capable of decomposing via two intermediates III and IV (Scheme A):

Scheme A

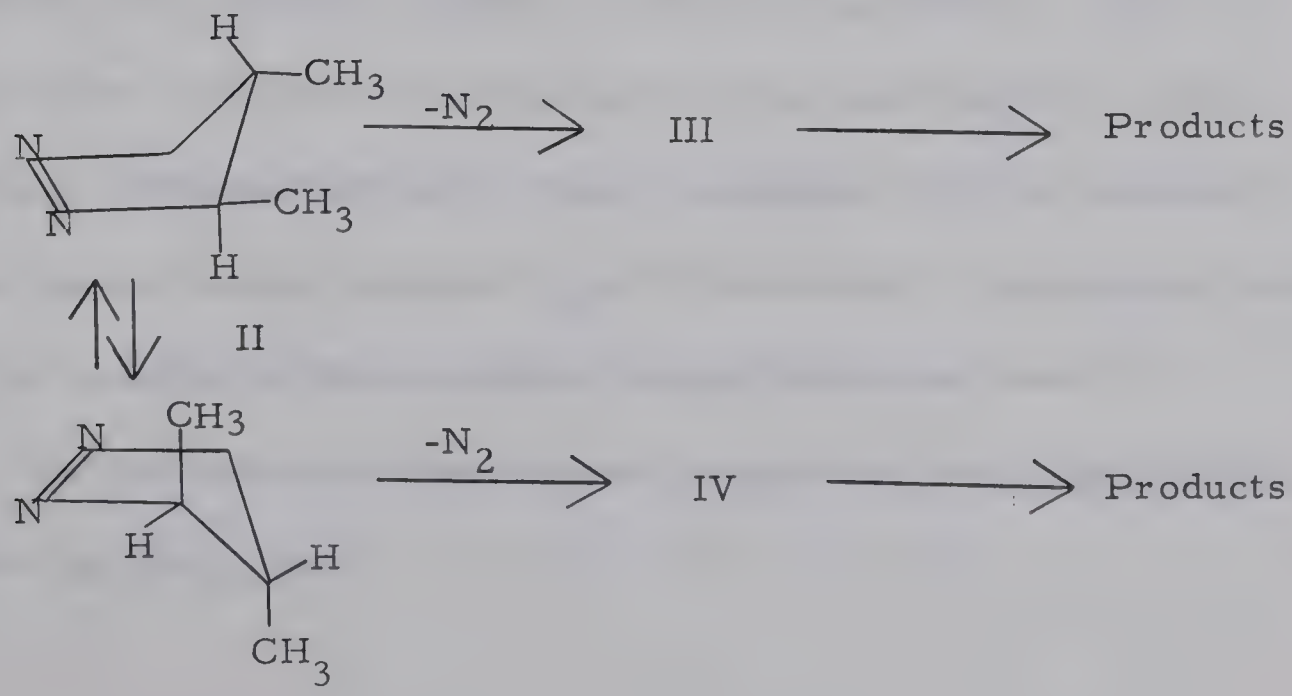


Previously we observed that olefins can be predicted to arise from each of these intermediates and as a result, the 2-methyl-2-butene provides a unique solution to the problem of what fraction of the cis-3,4-dimethyl-1-pyrazoline (I) thermolizes through intermediates III and IV. If we use I-d_2 the position of deuteration in the 2-methyl-2-butene produced is dependent upon the intermediate used, III or IV (see Scheme B).

Scheme B



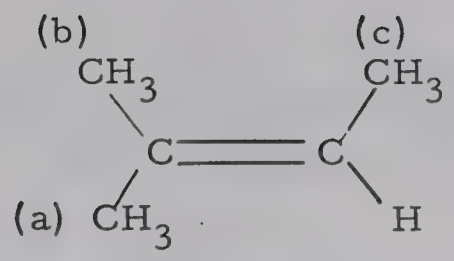
Scheme C



Thus the thermolysis of I-d_2 would produce trans-2-methyl-2-butene-1,1-d_2 (V) via the intermediate III, and cis-2-methyl-2-butene-1,1-d_2 (VI) via IV. Similarly II-d_2 would produce V or VI depending upon the preferred conformation in the transtition state (Scheme C). The 100 MHz nmr spectrum of 2-methyl-2-butene indicates a doublet at τ8.53 strongly coupled to the olefinic proton and a singlet at τ8.49 and at τ8.39. The assignment of the latter two peaks was made by the stereospecific synthesis of cis-2-methyl-2-butene-1,1,1,3-d_4 from 2-butanone-1,1,1,3,3-d_5 using Cornforth's elegant method[29]. Thus the methyl group cis to the hydrogen on C_3 was found to be the one at lowest field. Figures 17, 18, 19 and 20 show the 100 MHz spectrum of 2-methyl-2-butene, its -d_2 isomer coming from I-d_2, the other isomer coming from II-d_2 and the stereospecifically synthesized-d_4 isomer.

Careful integration of the nmr spectrum of 2-methyl-2-butene-d_2 indicated that the olefin derived from I-d_2 was greater than 94% VI, and II-d_2 produced 2-methyl-2-butene of greater than 96% V. Thus we conclude that I undergoes thermolysis via the intermediate IV and II goes via the intermediate III. This is consistent with the suggestion that the second methyl group at C_4 in 4,4-dimethyl-1-pyrazoline leads to steric crowding in the rate-determining transition state[13].

The calculations from the nmr integrations were conducted as follows e.g. II-d_2 case:



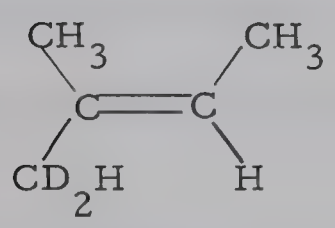
(a) at 8.39τ

(b) at 8.49τ

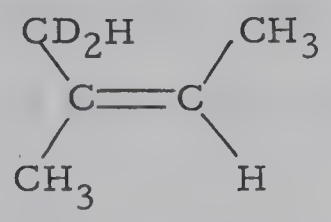
(c) at 8.53τ

Methyl group (c) is 50% hidden under (b).

The thermolysis will give V via intermediate III and VI via intermediate IV:



VI (n_B)



V (n_A)

$$R = \frac{I_1}{I_2 + I_3}$$

I_1 = integration of methyl group (a)

I_2 = integration of methyl group (b)

I_3 = integration of methyl group (c)

Taken into consideration that deuterium has no effect on the integration and the fact that methyl group (c) is half hidden under methyl group (b),

then:

$$R = \frac{3n_A + 1n_B}{1n_A + 3n_B + 1.5n_A + 1.5n_B + 1.5n_A + 1.5n_B}$$

$$= \frac{3n_A + (1 - n_A)}{1n_A + 3(1 - n_A) + 3} \qquad n_A + n_B = 1$$

Therefore:

$$R = \frac{2n_A + 1}{-2n_A + 6}$$

And:

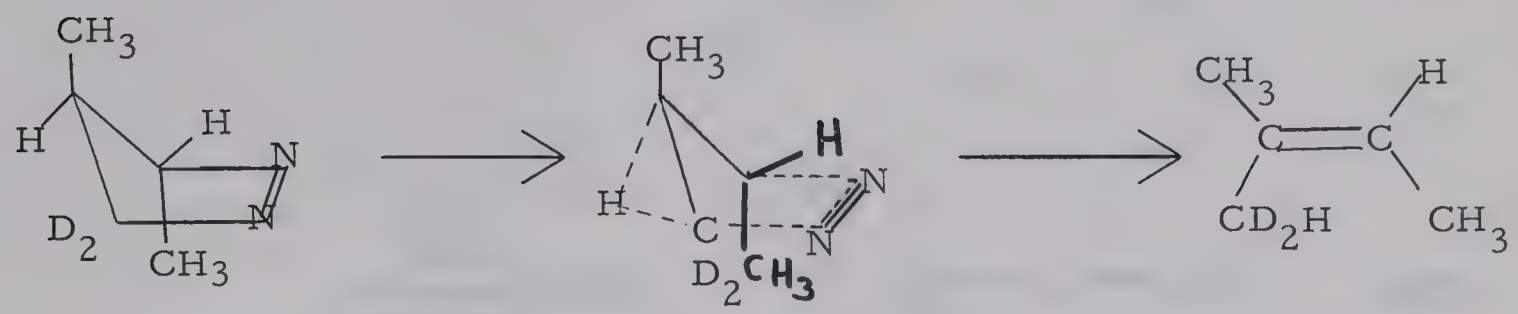
$$n_A = \frac{3R - 0.5}{1 + R} = \frac{2.1 - 0.5}{1.7} = 0.94$$

Because the pyrazoline II-d_2 was only about 96% deuterated, and the integration technique involves 3% error, then a correction for the result of the calculation will give 96 $\pm$ 4% of the isomer V.

E. Conclusion

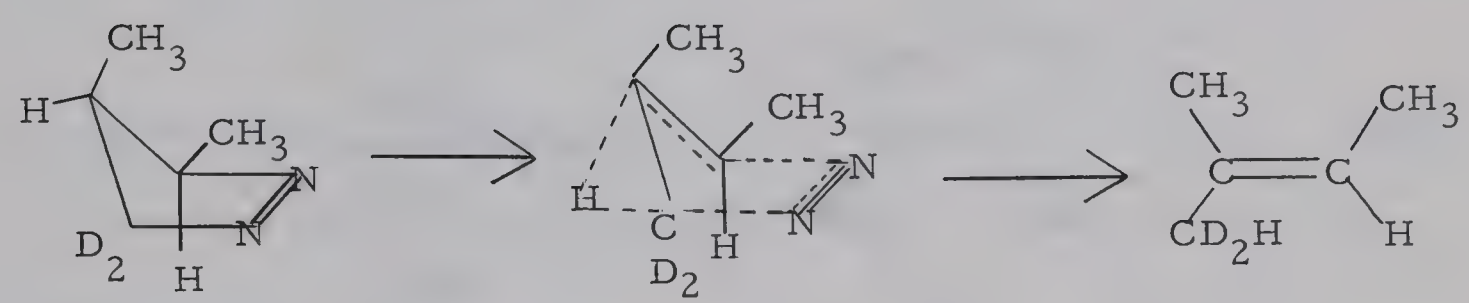
The thermolysis of I-d_2 gave rise to essentially 94 $\pm$ 4% of VI. Thus for all intents and purposes it appears that I thermolyzes exclusively through the intermediate III, and that II thermolyzes through intermediate IV. Since both intermediates III and IV are capable of giving significant yields of 2-methyl-2-butene, it may be said conclusively that neither III nor IV is capable of a stereospecific ring closure to cis- or trans-1,2-dimethylcyclopropane — a condition required of such intermediates if they are to play a role in the singlet methylene addition to cis- and

trans-2-butene. We may also note that the concerted hydrogen migration mechanism of MeGreer's[34] predicts the wrong isomers (see Scheme C).



II-d_2 VI

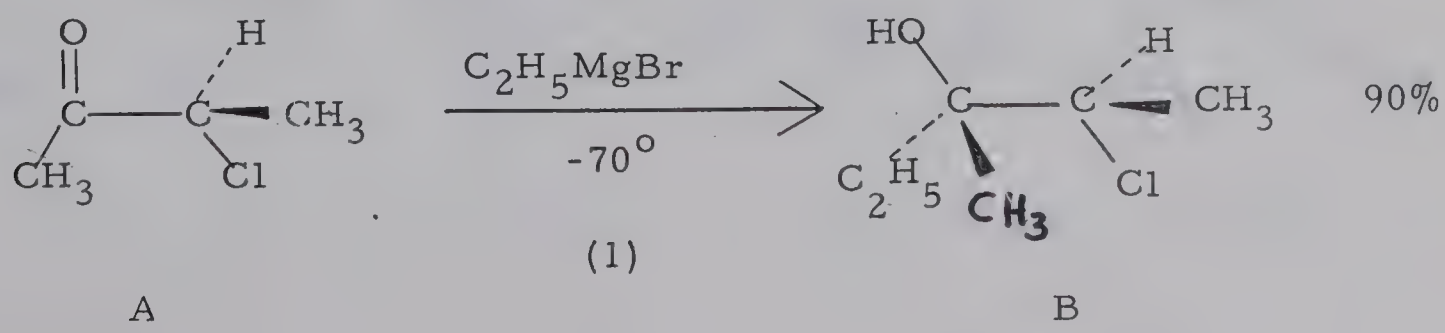
and



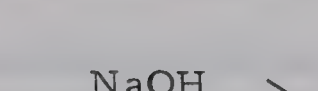
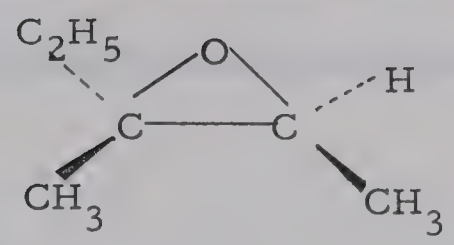
I-d_2 V

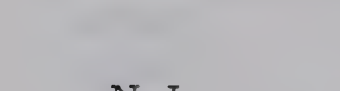
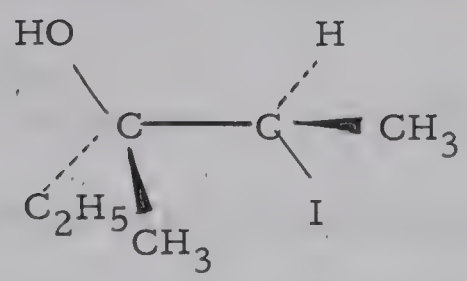
F. Cornforth's Scheme as a Method for Stereospecific Synthesis of cis-2-methyl-2-butene-1,1,1,3-d_4[29]

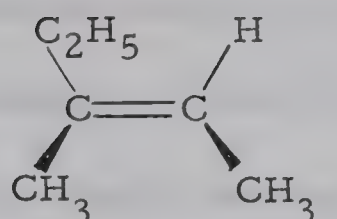
This scheme for the stereospecific synthesis of olefins is an excellent one for our purpose. The scheme could be represented in the following way, e.g. the compound 2-chloro-3-butanone (A):



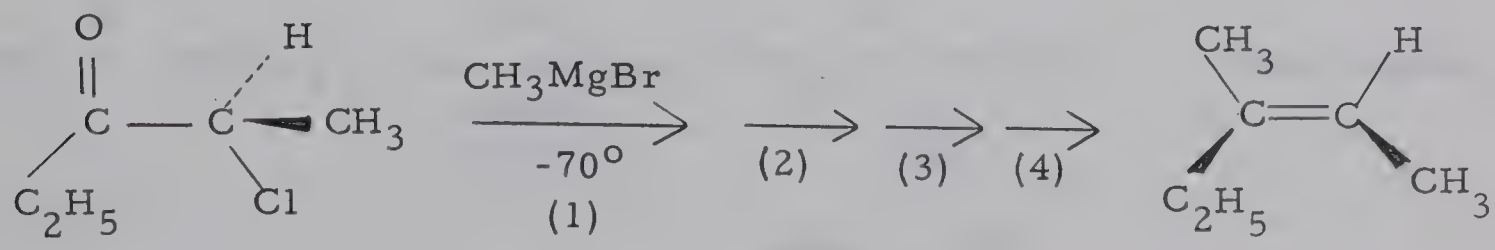
A (1) B 90%

B  (2)  C 91%

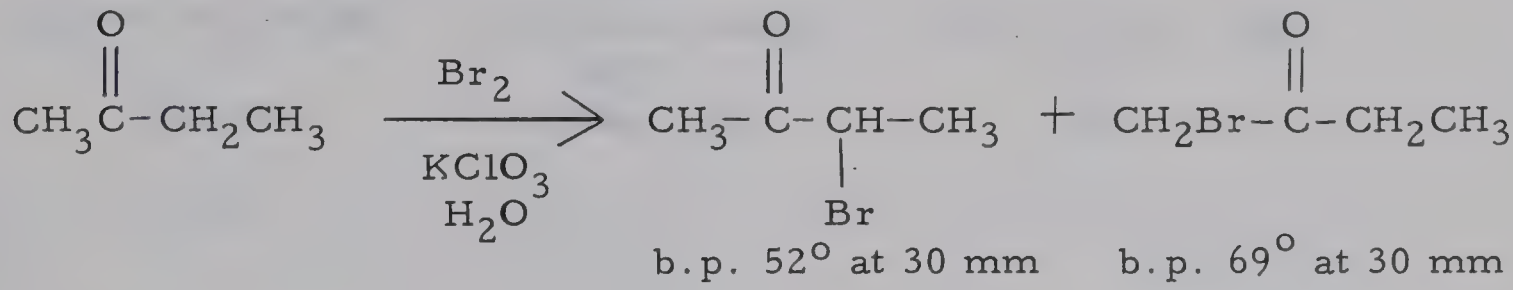
C  (3)  D 98%

D  (4)  E 81%

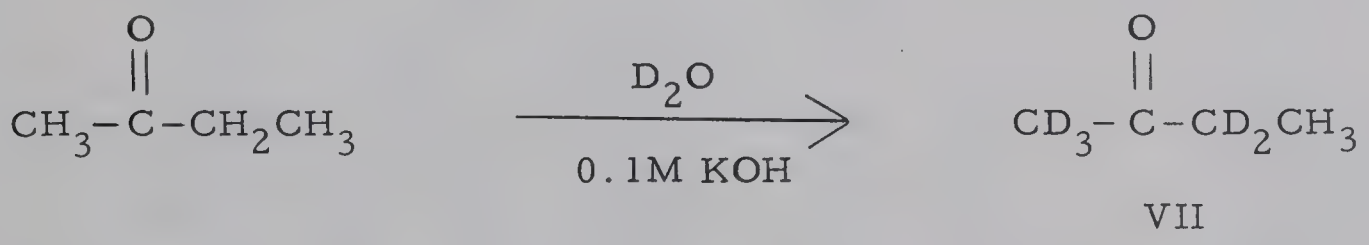
Notice that the ethyl group which was added with the Grignard reagent is <u>cis</u> to the olefinic hydrogen. Thus if one starts from 2-chloro-3-pentanone adding methyl magnesium bromide, he will end up with the <u>trans</u>-isomer of E.



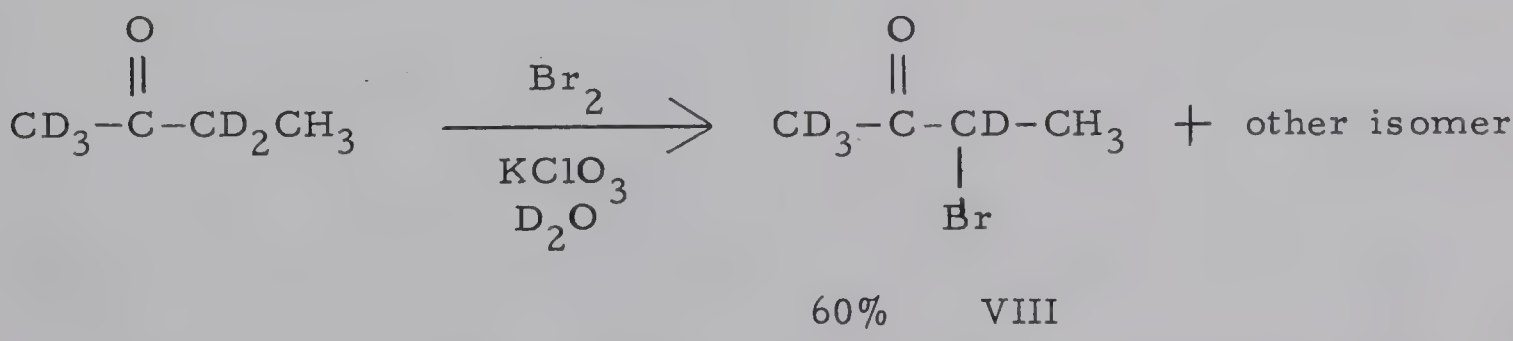
We used the same type of reaction on 3-bromo-2-butanone. This compound was synthesized from ethyl methyl ketone using the procedure of Catch[33]:



The low boiling isomer was separated by means of a spinning band column. The nmr of this compound is shown in spectrum number 14. The next step was to deuterate the α-haloketone before going to the Cornforth reactions. Unfortunately all attempts failed to do so. Thus it was necessary to deuterate the ethyl methyl ketone before the halogenation step.

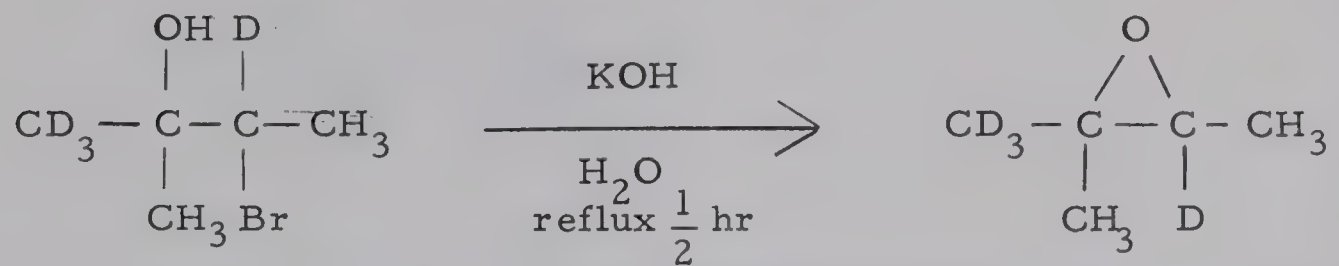


Bromination of VII using Catch's method gave 60% yield of 3-bromo-2-butanone-1,1,1,3-d_4 (VIII).



Since the procedure given by Cornforth to prepare the epoxide

from the chlorohydrin failed to give the epoxide with the bromohydrin, the procedure of Reed and Reid[32] was used:



IX X

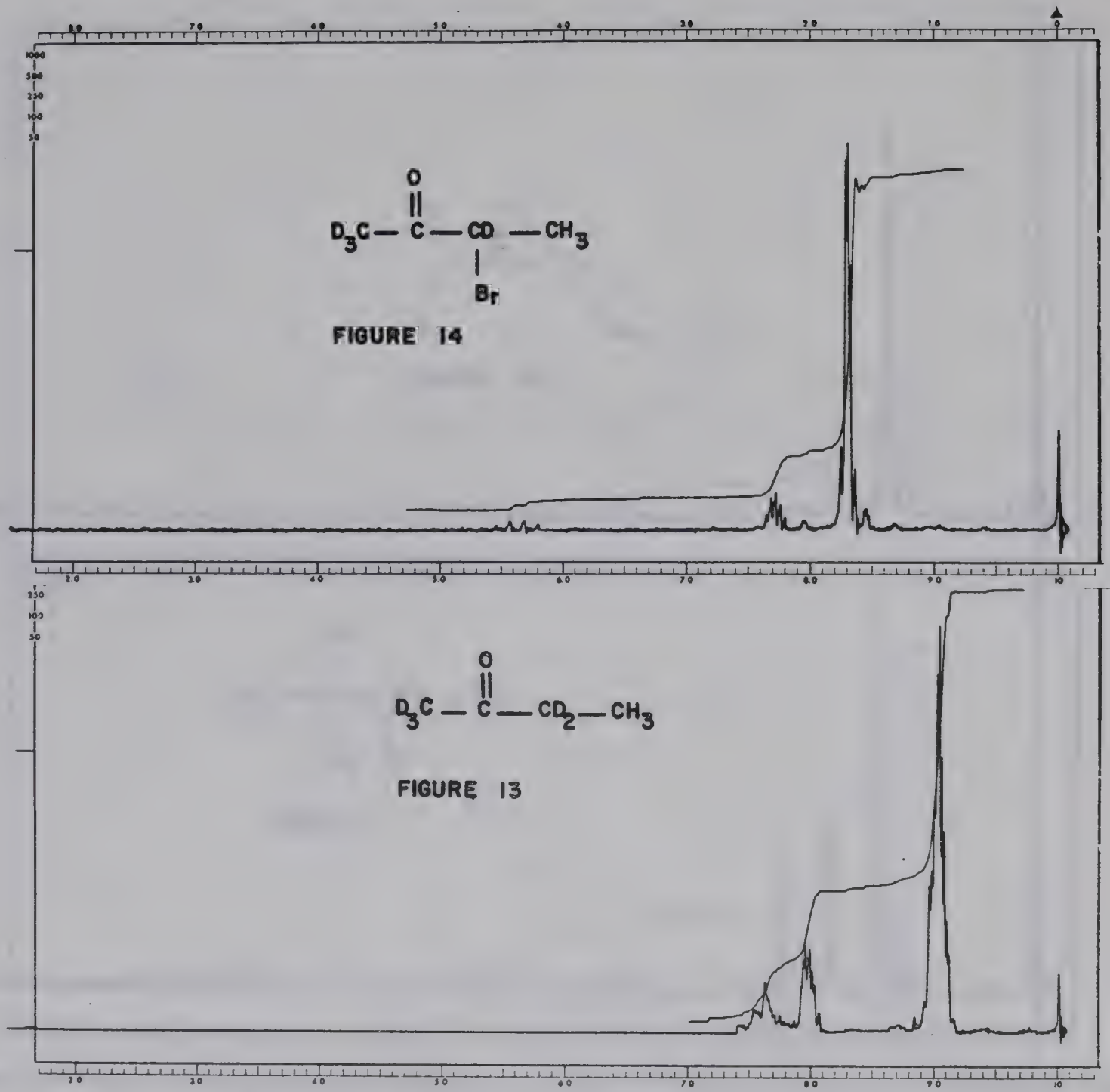
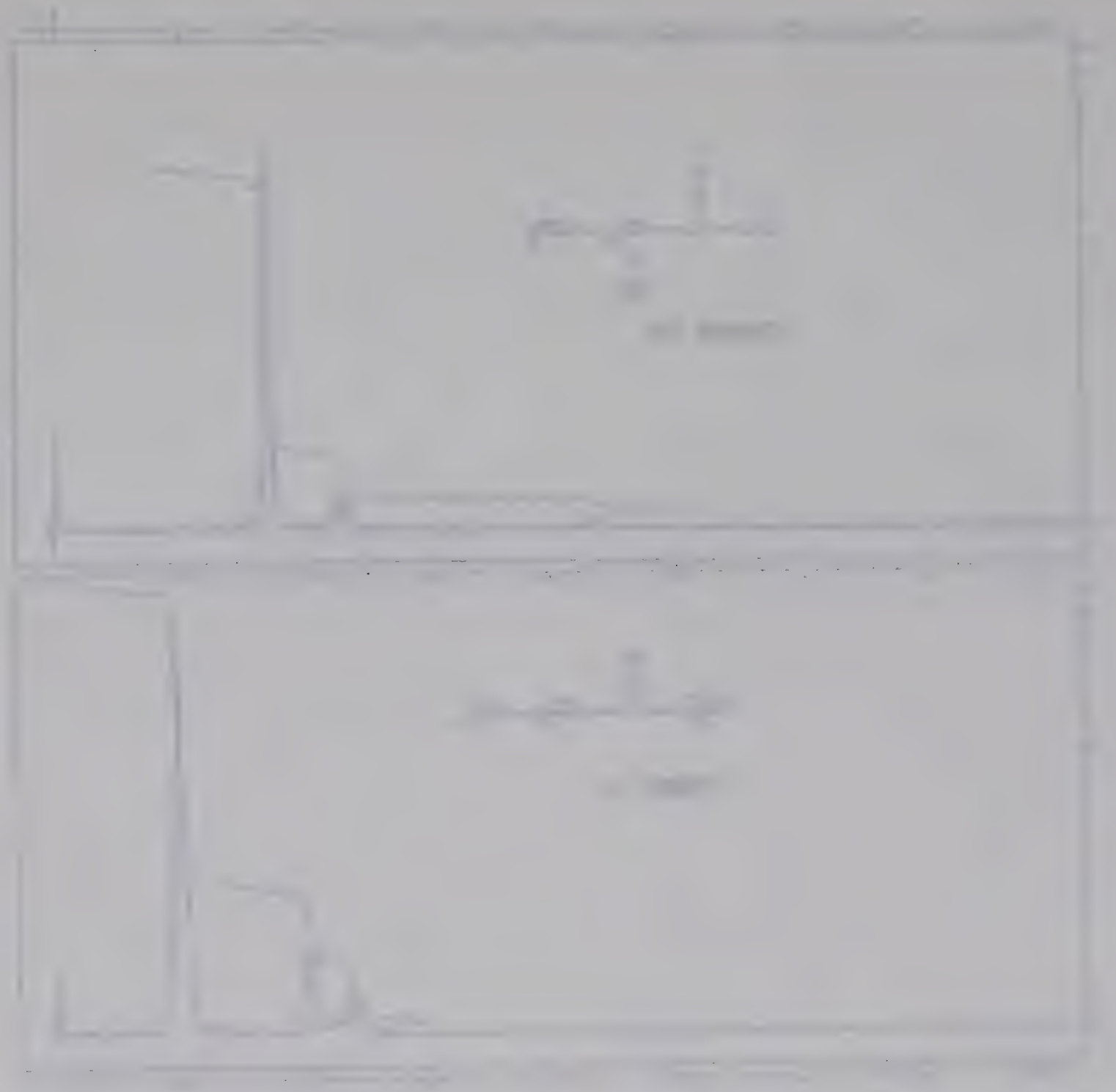


Figure 13 Nuclear Magnetic Resonance Spectrum of Ethyl Methyl Ketone-1,1,1,2,2-d_5 in Carbon Tetrachloride.

Figure 14 Nuclear Magnetic Resonance Spectrum of 3-Bromo-2-butanone-1,1,1,3-d_4 in Carbon Tetrachloride.



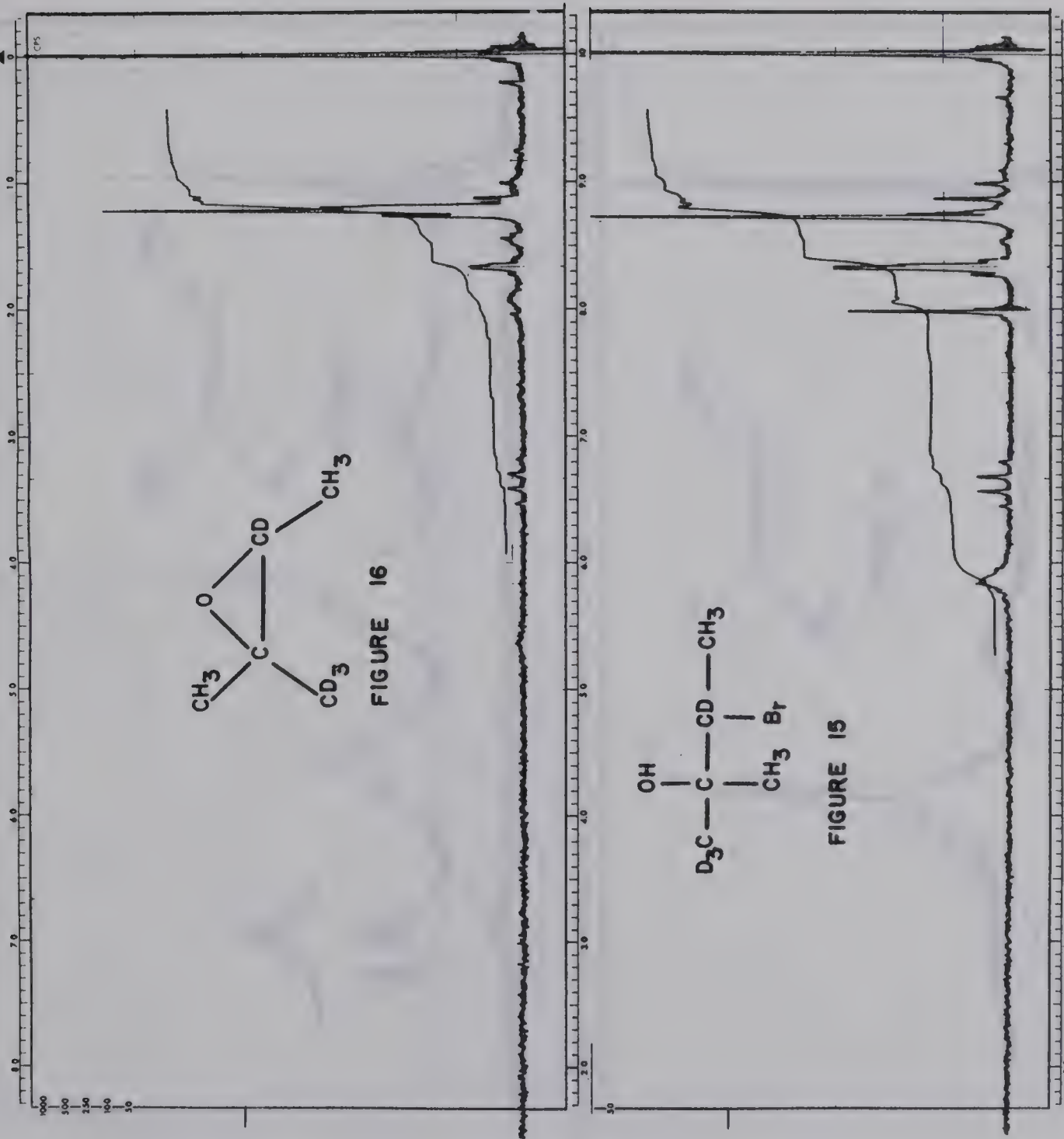
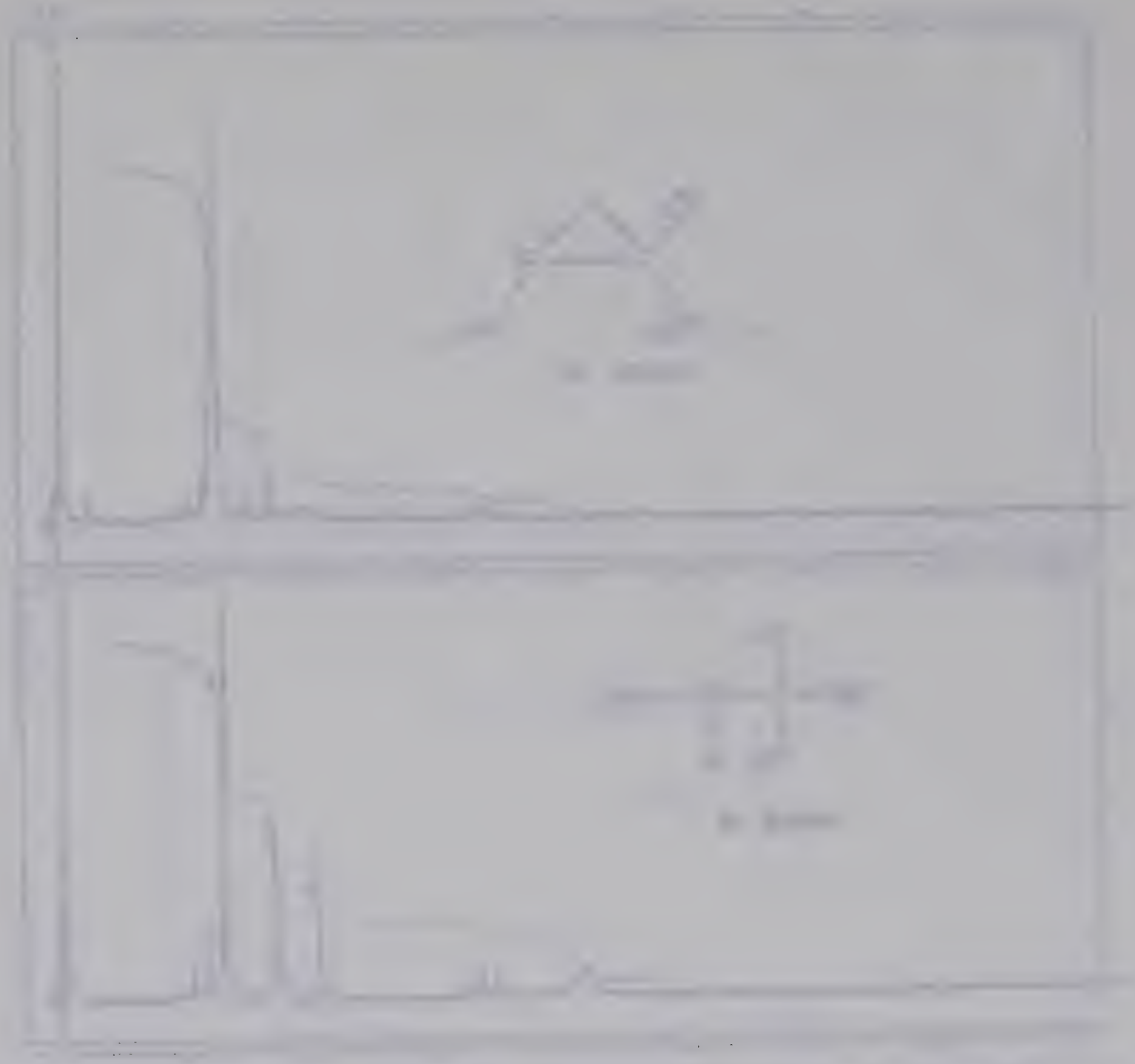


Figure 15 Nuclear Magnetic Resonance Spectrum of 2-Hydroxy-2-methyl-3-bromobutane-1,1,1,3-d_4 (Bromohydrin) in Carbon Tetrachloride.

Figure 16 Nuclear Magnetic Resonance Spectrum of trans-2:3-Epoxy-3-methylbutane-4,4,4,2-d_4 in Carbon Tetrachloride.



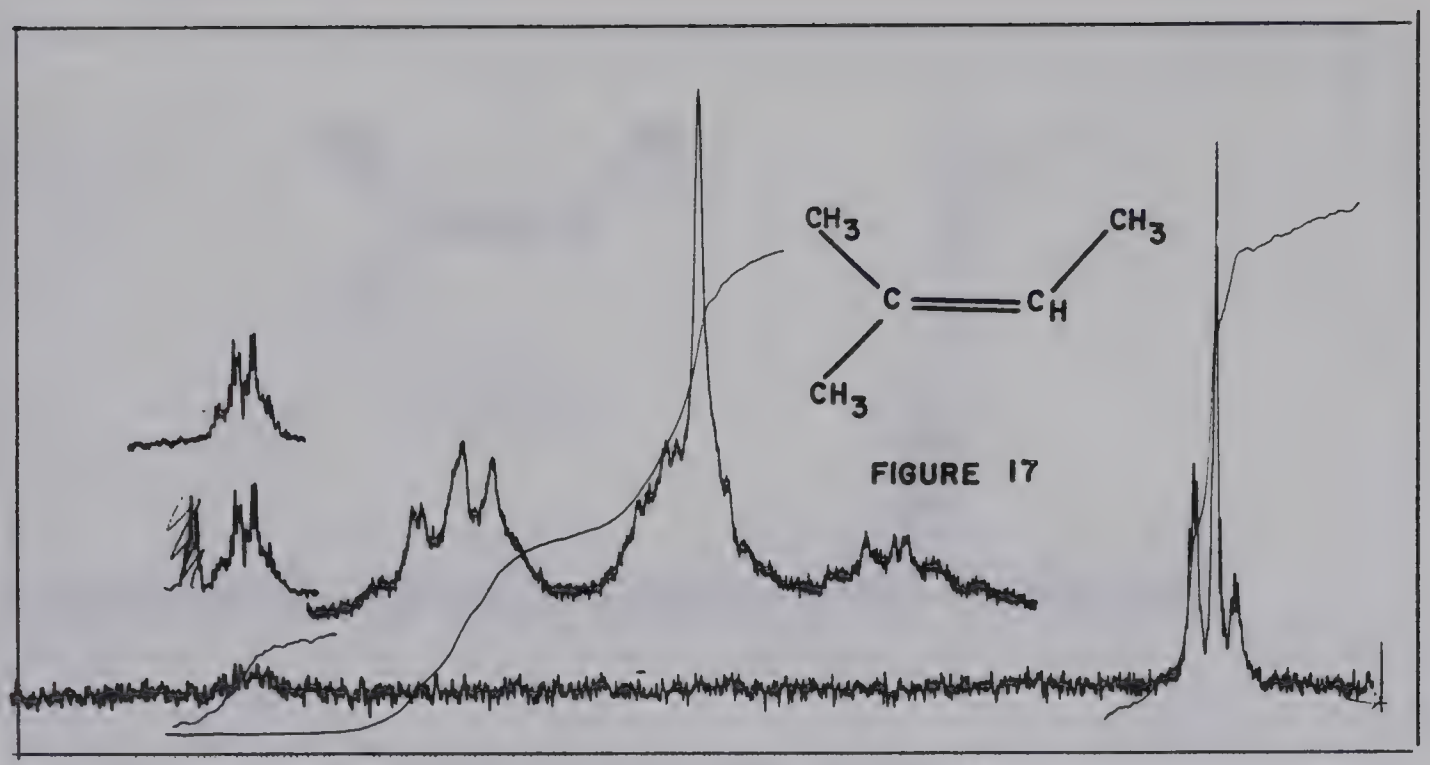


FIGURE 17

Nuclear Magnetic Resonance Spectrum of 2-Methyl-2-butene in Chloroform.

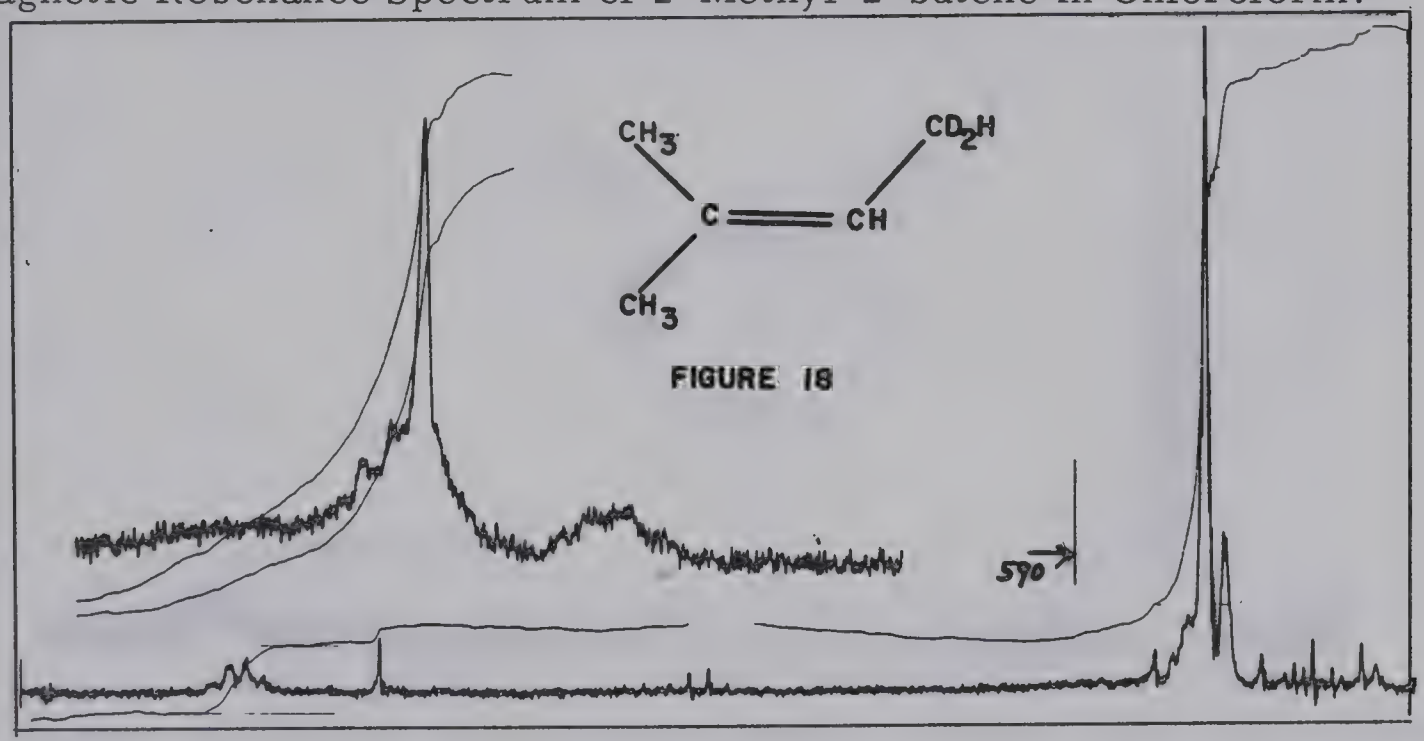
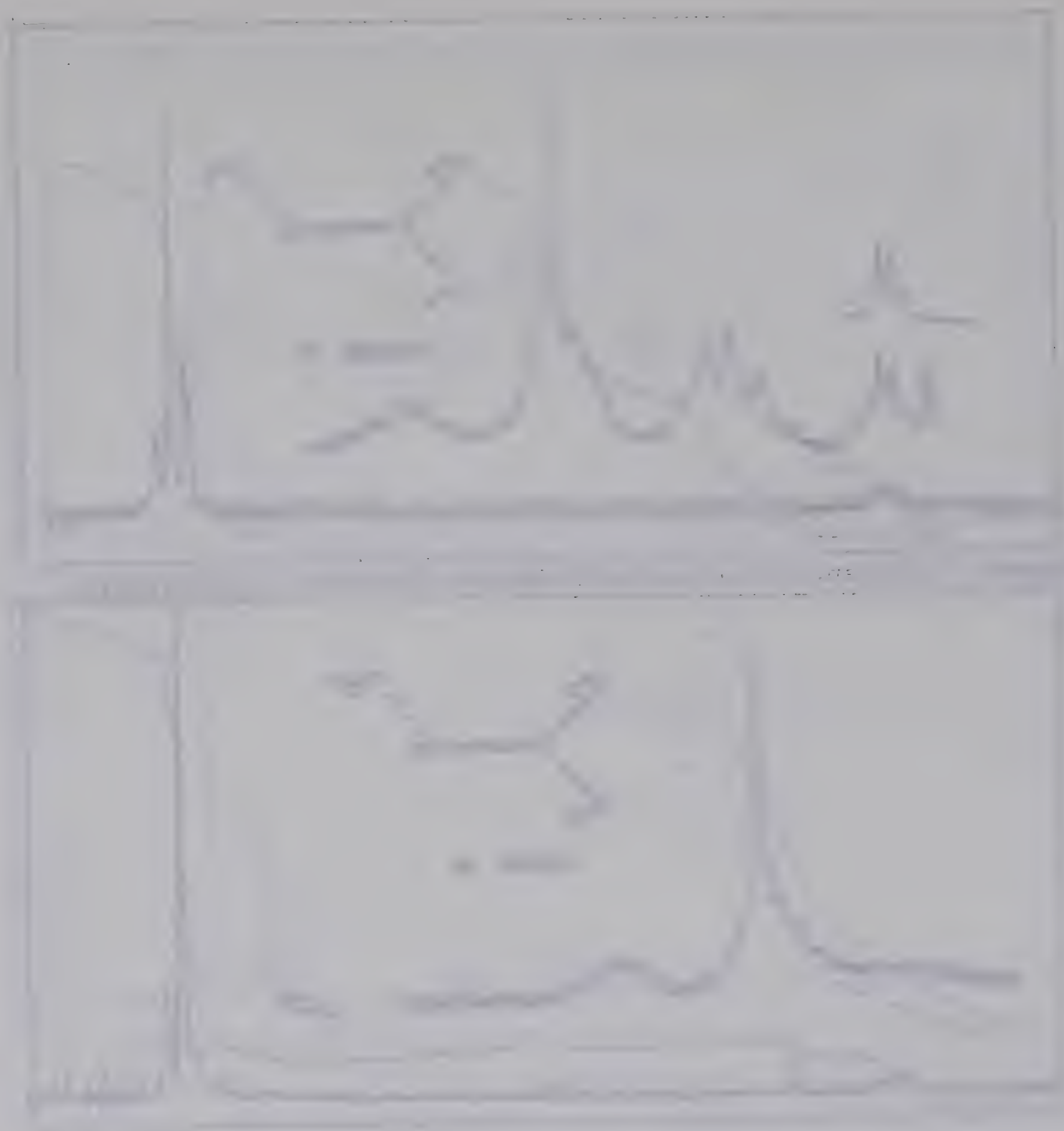


FIGURE 18

Nuclear Magnetic Resonance Spectrum of 2-Methyl-2-butene from Thermolysis of cis-3,4-Dimethyl-5,5-dideuterio-1-pyrazoline in Carbon Tetrachloride.



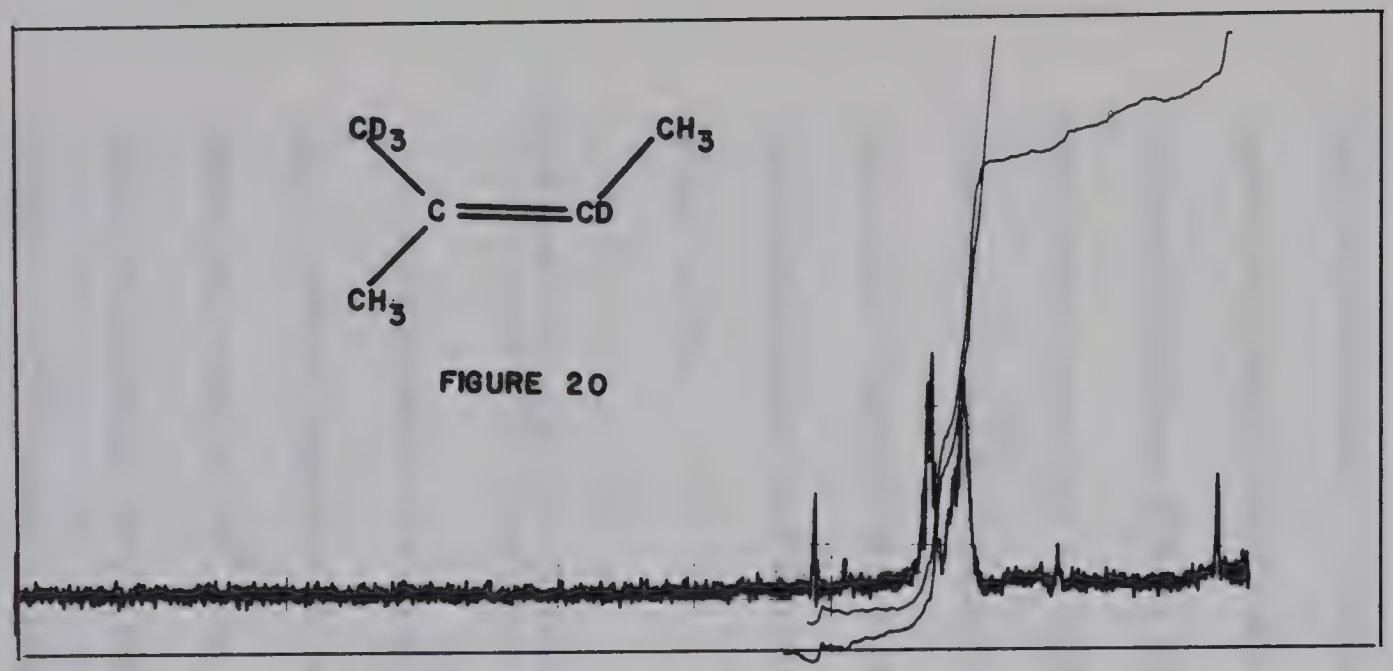


FIGURE 20

Nuclear Magnetic Resonance Spectrum of Stereospecifically Synthesized 2-Methyl-2-butene-1,1,1,4-d_4 in Carbon Tetrachloride.

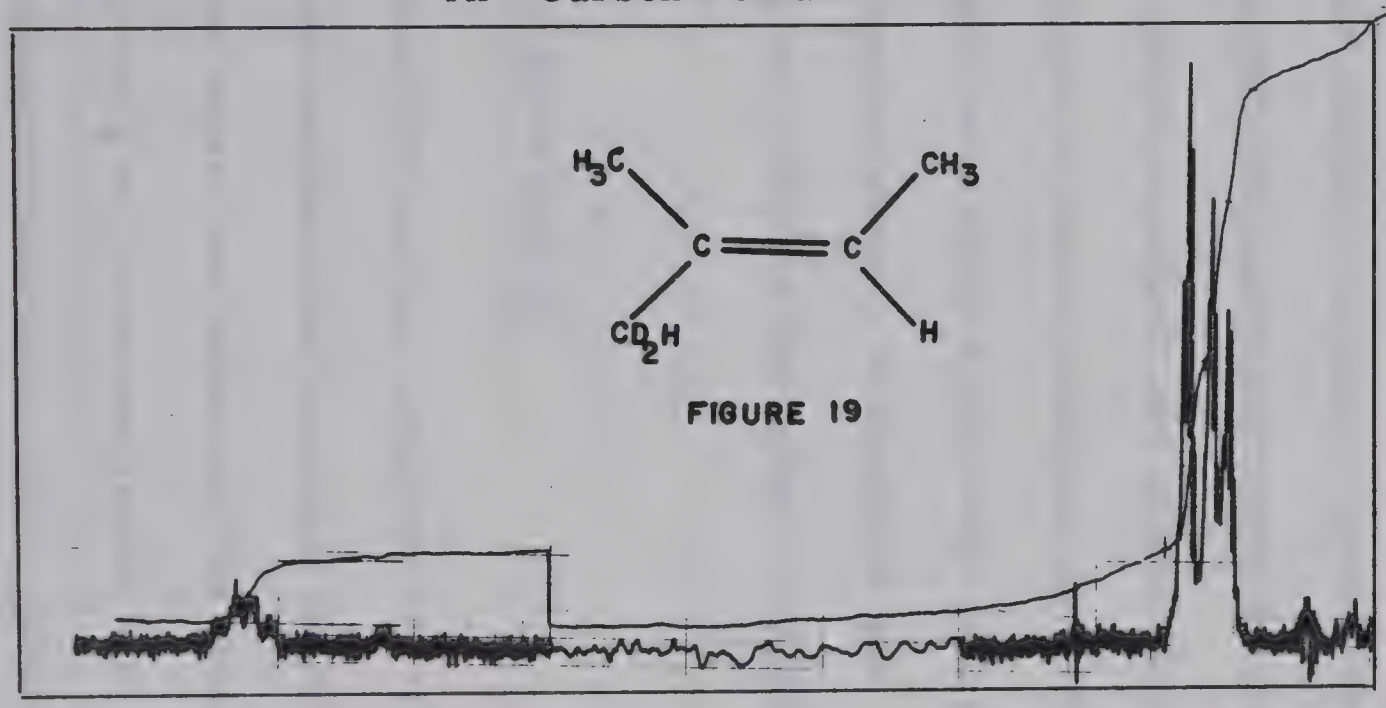
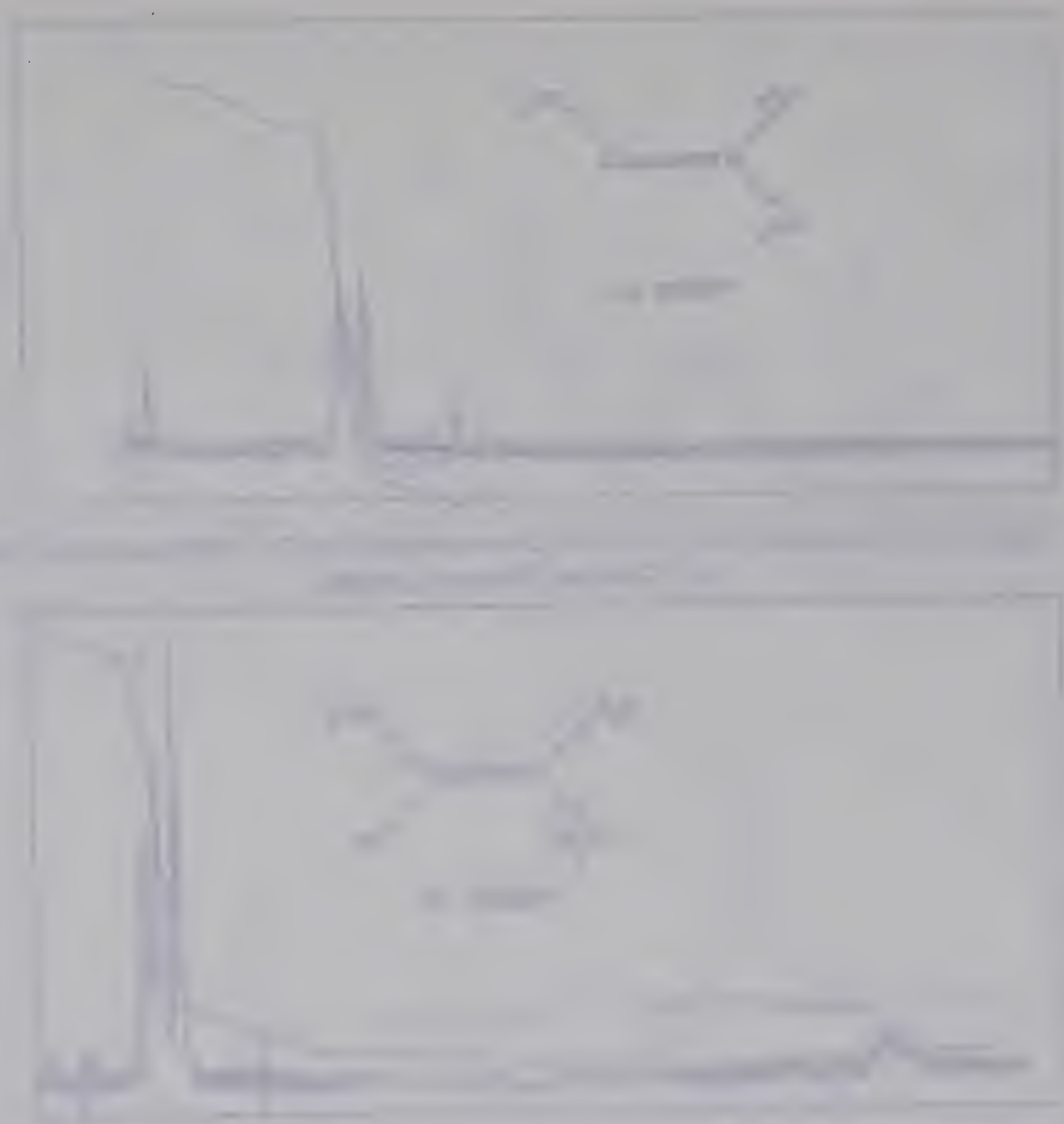


FIGURE 19

Nuclear Magnetic Resonance Spectrum of 2-Methyl-2-butene from Thermolysis of trans-3,4-Dimethyl-5,5-dideuterio-1-pyrazoline in Carbon Tetrachloride.



CHAPTER 4

EXPERIMENTAL SECTION

All boiling points are uncorrected. The infrared spectra were obtained on a Perkin-Elmer Model 421 spectrophotometer. The ultraviolet spectra were obtained on a Perkin-Elmer Model 202 spectrophotometer. The nuclear magnetic resonance spectra were measured using Varian A-60 and HR-100 spectrophotometers, using tetramethylsilane (TMS) as an internal standard, and unless otherwise mentioned were run as 20% solutions in carbon tetrachloride. The mass spectroscopic measurements were carried out using the high resolution Vickers MS-9 mass spectrometer. Preparative gas chromotography was carried out on a Wilkens Aerograph Autoprep Model A-700.

A. Synthesis of cis-3,4-Dimethyl-1-pyrazoline (I)

Diazomethane (6 g) in ether (150 ml) was added at -10° to dry cis-2-butene (approx. 75 ml) in a stainless steel pressure vessel. After one week at 40°, the cooled vessel was vented and the resulting liquid fractionally distilled to give 6 g of a colorless liquid; b.p. 32° (4 mm); n_D^{25} 1.4320. High resolution mass spectrometry gave a parent peak at 99.0848. Calculated for $C_5H_{10}N_2$, 99.0844.

The nmr spectrum of I is shown in Figure 5; the infrared

spectrum in Figure 1 and its ultraviolet spectrum in Figure 3.

A sample of high purity was obtained by preparative g.c. using a Ucon Insol (10%) on Fluropak support type column with a flow rate of 60 cc/min and temperature 118°. The retention time of the pyrazoline was 11 minutes.

One should avoid the presence of any carbon tetrachloride in this purification procedure. If any is present, it will pyrolyze in the injection port and will tautomerize over 70% of the 1-pyrazoline to 2-pyrazoline.

B. Synthesis of trans-3,4-Dimethyl-1-pyrazoline (II)

Application of the same procedure as used for cis-3,4-dimethyl-1-pyrazoline, only substituting trans-2-butene resulted in a product of b.p. 31.5° (4 mm); n_D^{25} 1.4286. Measured high resolution mass spectrum 99.0848 for $C_5H_{10}N_2$. Calculated 99.0844.

The nmr spectrum of II is shown in Figure 6; the IR spectrum in Figure 2; the UV spectrum in Figure 3.

A sample of high purity was obtained in the same way as that used for I.

C. Synthesis of cis- and trans-3,4-Dimethyl-1-pyrazoline-d_2 (I-d_2 and II-d_2)

The same procedure as was applied previously was used to prepare cis- and trans-3,4-dimethyl-5,5-dideuterio-1-pyrazoline

($I\text{-}d_2$ and $II\text{-}d_2$). That is by the addition of an ethereal solution of dideuteriodiazomethane to cis- and trans-2-butene.

Diazomethane was prepared by the method of Moore and Reed[30].

Dideuteriodiazomethane was prepared by base catalyzed deuterium exchange of diazomethane[31] with heavy water (D_2O).

D. Synthesis of cis-2-Methyl-2-Butene-1,1,1,3-d_4

(a) Procedure for the Deuteration of Ethyl Methyl Ketone:

A solution of 0.1M potassium hydroxide in deuterium oxide (50 ml) was added to ethyl methyl ketone (72 g) and was refluxed overnight. Next day the solution was cooled and potassium carbonate was added to a saturated solution. Layers were separated and another 50 g of 0.1M potassium hydroxide in deuterium oxide was added to the upper layer. The same thing was repeated three times. The nmr of the deuterated ketone showed over 80% deuteration which was enough for our purpose.

(b) Preparation of Methyl Grignard Reagent:

Methyl bromide (45 ml) was added dropwise to 16.5 g of magnesium in 250 ml ether. The reaction vessel was a 500 ml round bottom flask connected to an efficient reflux condenser and the reaction was carried out under nitrogen.

(c) Preparation of the ∝-Haloketone:

This compound was synthesized from ethyl methyl ketone using the procedure given by Catch[29].

(d) The Bromohydrin Preparation:

Methyl magnesium bromide (4 ml) prepared previously, was cooled to -70° and stirred during addition (10 min) of 5 ml of the ∝-halocarbonyl compound (VIII) dissolved in a little ether. After 10-15 min a slight excess of acetic acid in ether was added; the mixture was brought to room temperature and diluted with water. The aqueous layer was extracted once with ether and the combined ethereal solutions were washed with water, aqueous sodium bicarbonate and water. From the dryed ($MgSO_4$) solution, the bromohydrin was isolated by distillation, b.p. 57-58° at 15 mm. The nmr of the bromohydrin (IX) is given in spectrum number 15.

(e) Preparation of the Epoxide:

This was prepared using the procedure of Reed and Reid[32].

The bromohydrin (3-bromo-2-methyl-2-butanol) (13 g) was added to KOH (4.5 g) dissolved in 37.5 ml H_2O, the mixture being heated for 1/2 hr on the water bath (reflux) with frequent shaking. After the upper oily layer had been separated, the aqueous liquid was distilled until no more oil passed over; upon adding the distillate to

the oily layer, drying the mixture with anhydrous Na_2SO_4 and distilling it, the whole (3.2 g) passed over at 74-78°; n_D^{18} 1.3896.

(f) Stereospecific Reduction of Iodohydrin from trans-2:3-Epoxy-3-methylbutane-4,4,4,2-d_4:

The epoxide (VIII) (0.95 g) was added to a cooled (-20°) solution of sodium iodide (2.5 g) and sodium acetate (0.25 g) in acetic acid (5 ml) and propionic acid (10 ml). After 30 min the mixture was warmed to room temperature and poured into ether and aqueous sodium hydrogen carbonate. The ether was washed with a little sodium hydrogen sulphite and with water, dryed ($MgSO_4$), and evaporated at low pressure. The iodohydrin (1.5 g) was added to a cooled (0°) solution of anhydrous stannous chloride (4 g) in pyridine (15 ml). Phosphoryl chloride (1 ml) in pyridine (3 ml) was then added with cooling. The mixture solidified after a few minutes. Next day, water was added and the olefin was distilled. The receiver was kept at -10°. The distillate (0.5 g) was chromatographed in a g.c. apparatus using a 10 ft. 20% DMS on Fluoropak column at room temperature and 20 cc/min flow rate, helium was used as the carrier gas. The olefin peak was trapped in liquid nitrogen (retention time was 11 min) and its 100 MHz nmr spectrum was obtained (see spectrum number 20).

E. Kinetic Procedures

(a) The Thermolysis of the Pyrazolines:

1,3,5-Triethylbenzene was used as the refluxing liquid, and the glass bulbs containing the pyrazolines were hung in its vapour. This liquid boils at 218° which was a suitable temperature for the thermolysis. After three hours, the bulbs were removed, and were broken inside a bulb crusher which was a part of a g.c. apparatus.

(b) Kinetic Measurements:

The reactor system for the kinetic measurements was the same as designed by Smith et al[25] and as was slightly modified by Crawford[27]. The thermocouple used for measurement of temperature was a four-junction chromel-alumel type. A diagram of the experimental arrangement for the kinetic measurements is shown in Figure 21.

F. Product Analysis and Identification

(a) The Bulb Crusher:

A schematic diagram of the bulb crusher, used to study the products by g.c., is shown in Figure 22. A could be fitted into B and the chamber C completely closed by screwing the top of A into that of B. B was preheated by means of electric heating tape wound

Figure 21

Schematic diagram for the arrangement of kinetic measurements in the thermolysis of 1-pyrazolines.

A = Reactor

B = Relay

C = Manometer

D = Small Ballast

E = Nitrogen Tank

F = Big Ballast

G = Transducer

H = Diaphragm

J = Ice-water cold junction

K = Potentiometer

L = Thermocouples

M = Heaters

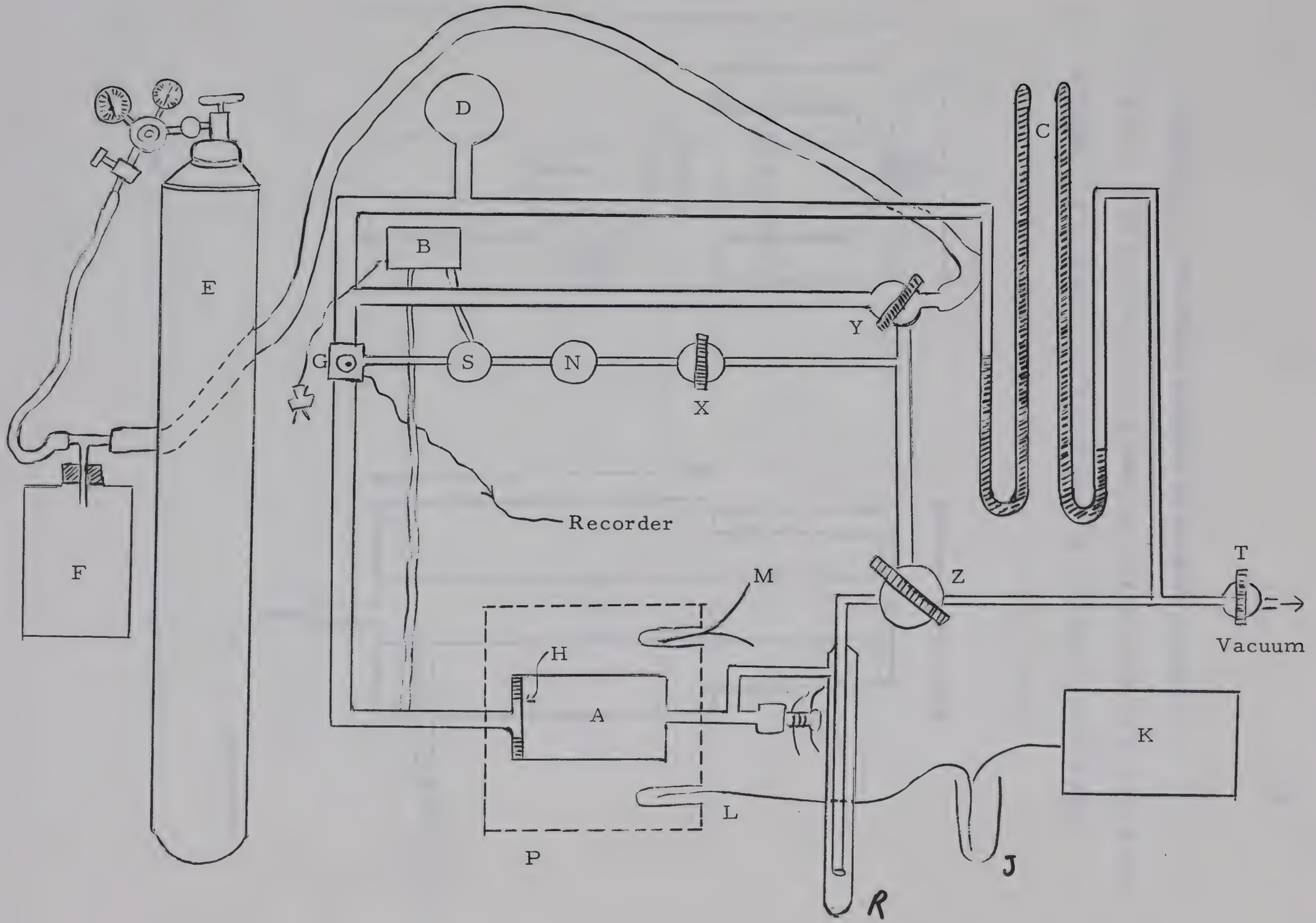
N = Needle Valve

P = Glass-wool insulation

R = Cold Trap

S = Solenoid Valve

T, X, Y, Z, = Stopcocks


D
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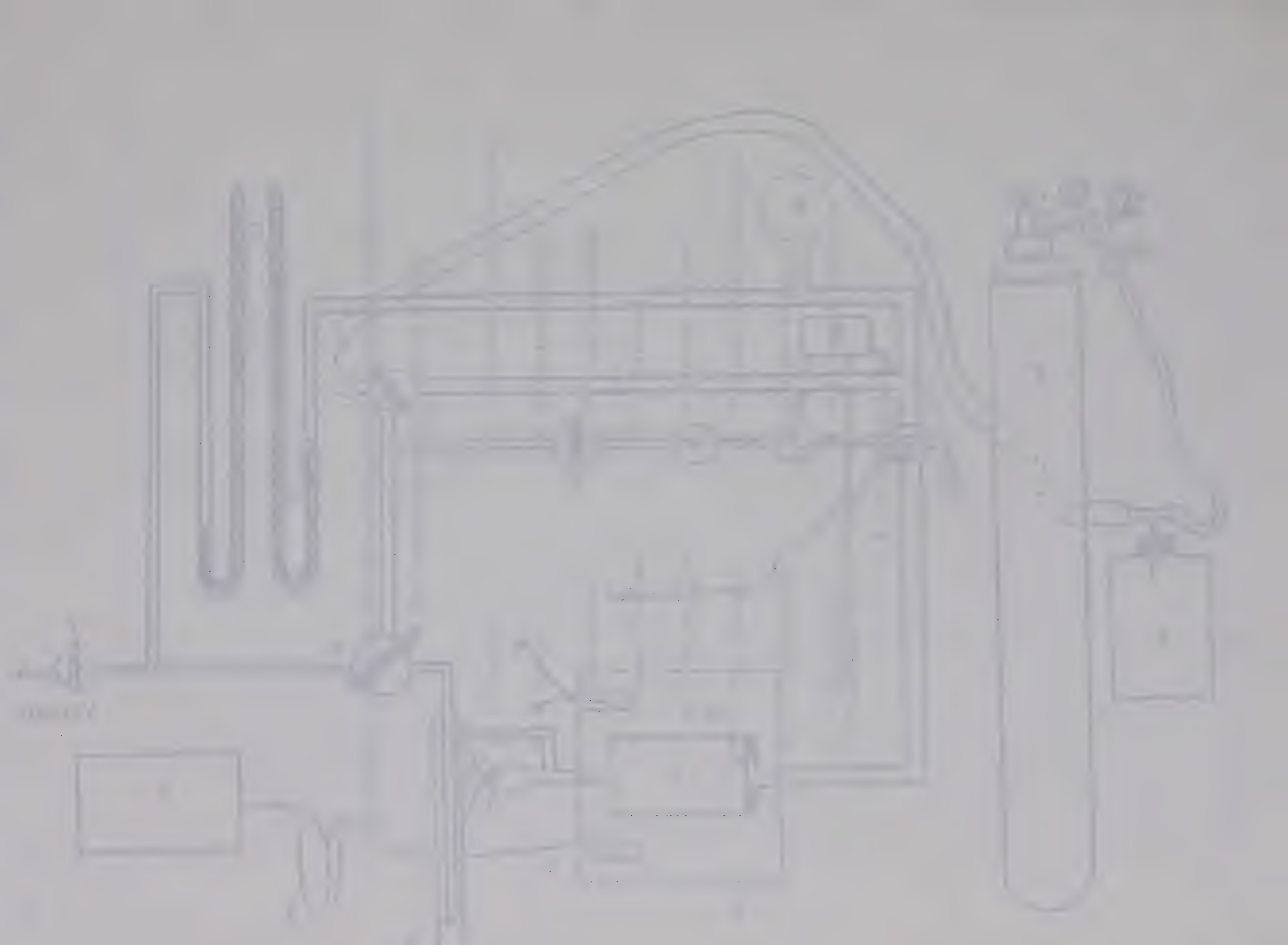
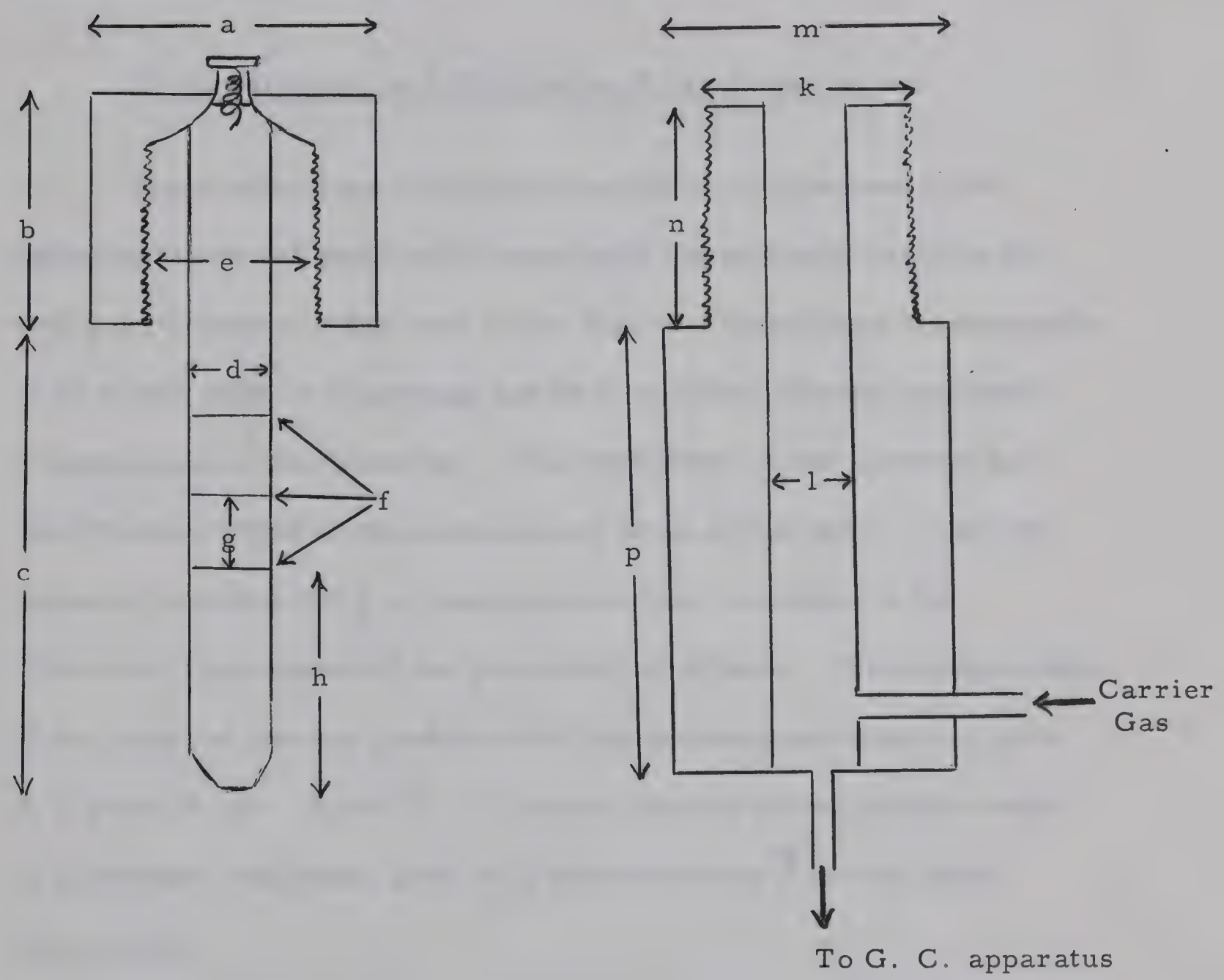
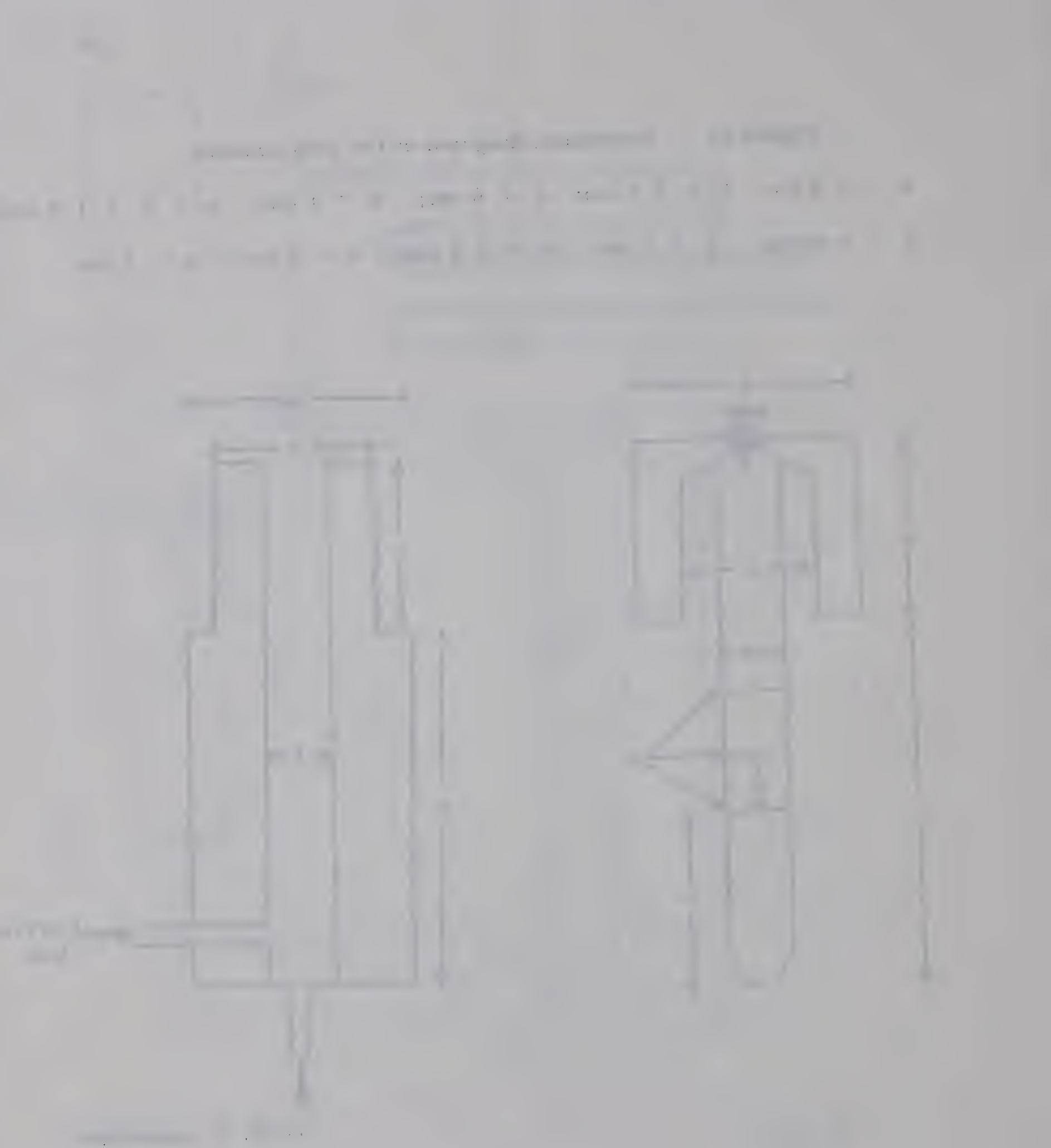


Figure 21 Schematic diagram of the bulb crusher.

a = 2.5 cm; b = 2.5 cm; c = 6 cm; d = 1 cm; e = k = 1.8 cm; f = o-rings; g = 1 cm; h = 2.5 cm; n = 2 cm; p = 7 cm.





around it, and the temperature inside C was maintained at about 170°C. The bulb to be broken was put inside C, which was subsequently closed and then helium was allowed to flow through it. When the system was at equilibrium, the bulb was crushed and the product analyzed by conventional g.c. methods.

(b) Identification and Estimation of the Products:

The products were identified mainly by comparison of the retention times and peak-enrichment with the authentic samples on four g.c. columns. The best of the four was found to be a combination of 10 ft 20% DMS on Fluoropak and 24 ft of silver nitrate-saturated propylene glycol on firebrick. The conditions of the columns and the retention times of the products are given in Table III. All the authentic samples for g.c. comparisons were available at the Chemistry Department of the University of Alberta. The comparisons of the infrared spectra products with the authentic samples are given in Figures 9, 10, 11 and 12. The nmr spectra of the products were in agreement with those given in a previous work[27] for the same compounds.

G. Isolation of 2-Methyl-2-butene from the Thermolysis of Deuterated Pyrazolines

A special spiral trap 10 ft in length was connected to the reactor

arrangement of the kinetic measurements (see the diagram Figure 21, between T and the vacuum). The products of the thermolysis from three injections (50 microliters each) were trapped in the spiral using liquid nitrogen as the cold bath. The spiral was closed and then removed. In a special g.c. arrangement, the spiral trap was connected between the cylinder of the carrier gas (helium) and the g.c. column suitable for the analysis. The g.c. column used and the conditions were those mentioned in the identification part. The peak of the compound (retention time 16.8 min) was collected in a trap, liquid nitrogen was used as the cold bath. The trap was quickly connected to a vacuum rack, and through alternate melting and freezing, the sample was introduced into an nmr tube which was subsequently sealed using 20% chloroform in deuteriochloroform as a reference.

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